Patent Abstracts of Japan

02-3-180-A WO

PUBLICATION NUMBER : 63317297
PUBLICATION DATE : 26-12-88

APPLICATION DATE : 22-06-87
APPLICATION NUMBER : 62154967

APPLICANT : KANTO YAKIN KOGYO KK;

INVENTOR : TAKAHASHI SUSUMU;

INT.CL. : B23K 35/363 B23K 3/04

TITLE : DIP BRAZING METHOD FOR ALUMINUM OR ITS ALLOY MEMBER

ABSTRACT : PURPOSE: To easily clean a flux and to join the surface of ah Al brazing member in a brightening state by using the flux of the composition made by specific $BaCl_2$, NaCl, KCl and fluoride.

CONSTITUTION: The powder of 55~47% BaCl, 18~22% NaCl and 27~33% KCl by weight ratio is melted in an electrode furnace and held at specified temp. by mixing the fluoride of 1~20% weight ratio therewith. The Al-Si base aluminum alloy brazing junction member preheated at the specified temp. in an air atmosphere electric furnace is thereafter dipped in a molten flux and taken off after holding it with its temp. rise. The flux is then removed by the cleaning by air cooling, hot water washing and a detergent to clean the member surface. As a result in brazing the whole joining part forms a sufficient fillet and a strong joining part is obtainable.

⑲日本国特許庁（JP）　⑪特許出願公開
⑫公開特許公報（A）　昭63-317297

⑤Int.Cl.⁴　識別記号　庁内整理番号　㊸公開　昭和63年(1988)12月26日
B 23 K 35/363　G-6919-4E
3/04　X-6919-4E

審査請求　有　発明の数　1　（全3頁）

⑤発明の名称　アルミニウム又はその合金部材の浸漬ろう付け法

㉑特　願　昭62-154967
㉒出　願　昭62(1987)6月22日

⑫発明者　高橋　進　神奈川県横浜市保土ケ谷区藤塚236-50
⑪出願人　関東冶金工業株式会社　神奈川県平塚市四之宮2543番地
⑭代理人　弁理士　浅賀　一夫　外1名

明　細　書

1．発明の名称

アルミニウム又はその合金部材の浸漬ろう付け法

2．特許請求の範囲

あらかじめろう材をつけたアルミニウム又はその合金部材を、55～47重量%の塩化バリウムと18～22重量%の塩化ナトリウムと27～33重量%の塩化カリウムと1～20重量%のフッ化物とからなる溶融フラックス中に浸漬してろう付けする方法であって、該溶融フラックスはろう付け前に直流電解して必要に応じ浄化してなることを特徴とするアルミニウム又はその合金部材の浸漬ろう付け法。

3．発明の詳細な説明

（イ）産業上の利用分野

本発明は、アルミニウム又はその合金部材の浸漬ろう付け接合法に関するものである。

（ロ）背景技術

従来からの浸漬ろう付けは、一般に塩化ナトリウム，塩化カリウム，塩化リチウムならびにフッ化アルミニウム等のフッ化物からなるフラックスを耐火物槽中に溶融し、組立てられたろう付け部材を該溶融液中に浸漬して、接合部にあらかじめクラッドされるか又は置かれたろう材を溶融させて接合部材を接合するもので、溶融フラックスはその本来の役割であるフラックス効果の他に無酸化加熱雰囲気と無酸化加熱媒体を構成するものである。

これらのことから、浸漬によるろう付け接合方法は、加熱炉によるろう付け法等に比して昇温速度が早くかつ均一加熱が容易で、ろう付けの信頼性が高いという特徴を有している。

ところが、ろう付け温度と整合するフラックス溶融温度，流動性アルミニウムの表面清浄力ならびにろう材の流れ誘導などの諸性質を持たせるために開発されたフラックス（塩化ナトリウム，塩化カリウム，塩化リチウム，フッ化物など）は潮解性が強く、鋼や銅などの金属を強く腐食し、また導電性であるので電気機器の絶縁を破壊する欠

点がある。

フラックスの潮解性は、ろう付け温度の580～620℃においても、フラックス中に水分が存在してアルミニウムを激しく酸化させ、ろう付けを阻害する。

このため、溶融フラックスはあらかじめ表面の浄化されたアルミニウム板をフラックス中に浸漬して水と反応させ、水素と酸化アルミニウムとして脱水する必要がある。また、溶融フラックスは長時間にわたる空気との接触が避けられず、脱水作業を繰り返し行なう必要がある。しかも、脱水作業でできた酸化アルミニウムなどの沈殿物の除去作業も欠かせない等の問題があった。

（ハ）発明の開示

本発明は、潮解性のないフラックスによる浸漬ろう付け法を提案するものである。

即ち、本発明は潮解性を持たない塩化バリウム（BaCℓ₂），塩化ナトリウム（NaCℓ）ならびに塩化カリウム（KCℓ）を主とし、これにフッ化物を加えて、化学活性化のあるフラックスとしたものである。

例えば、BaCℓ₂，NaCℓ及びKCℓの重量比がそれぞれ54.7：18.0：27.3 の共融塩の融点は540℃である。またアルミニウム硬ろうのAℓ－Si基合金の溶融温度が564～580℃であり、ろう付け作業温度が580～615℃であることから、上記共融塩の溶融温度の540℃はアルミニウム又はその合金のろう付けフラックスとして適当である。

また、フラックスの化学的活性化のために、フッ化物例えばフッ化アルミニウム（$AℓF_3$）やフッ化ナトリウム（NaF）などを混合するが、この場合に混合によるフラックスの溶融温度は570℃好ましくは565℃まで昇温してもよいので、上記共融塩が540℃であるから、30℃（又は25℃）の余裕がなおあることとなる。これは、フッ化物の種類と量の選択に幅があり、また共融塩の混合比にも幅を持たせることができることになる。

この場合、塩化バリウム，塩化ナトリウム，塩化カリウム及びフッ化物の重量比の範囲は、それぞれ55～47％，18～22％，27～33％，1～20％である。

従って、従来の塩化物フラックスを用いた場合と異なって、本発明の方法に用いられるフラックスは潮解性がないために溶融フラックス中の水分の脱水作業を行なう必要はないが、長時間の運転作業中に溶融フラックス中に生じる微量の不純物（金属，水分，酸素等）を除去して、より高精度のろう付けを保証する必要がある。

このため、本発明は直流電解法によりこれらの不純物を容易にかつ必要に応じて除去する方法を提案するものである。

（ニ）実施例

実施例1

BaCℓ₂，NaCℓ及びKCℓの粉末を重量比で54.7％，18.0％，23.3％と、これに重量比10％のNaF粉末を混合し、黒鉛電極を炉内槽底部に対向して設けられた耐火レンガ製電極炉で溶融し、610℃±3℃に保持し、空気雰囲気電気炉で560℃±5℃に予熱したAℓ－Si基のアルミニウム合金ろう付け接合部材を該溶融フラックス中に浸漬し、610℃に昇温して3分間保持後に取出した。その後、空冷，湯洗，洗浄剤による洗浄でフラックスを除去し、部材表面を清浄化した。

ろう付けの結果は全接合部が充分なフィレットを形成し、強固な接合部材が得られた。

さらに、12時間後と24時間後に上記したところと同様に事前の脱水作業を行なうことなく同一の電気炉中で浸漬ろう付けを行なったが、上記と同様に良好な接合が得られた。

また、電気炉から昇る蒸気はベタついておらず、蒸気も潮解性のないものであって、作業環境に悪影響を与えないことも認められた。

上記したろう付け作業を更に引続き行ない運転を重ねたところ、ろう付け時にアルミニウム合金ろう付け接合部材の表面に黒色付着物が認められるに至った。

そこで、ろう付けを中断して、フラックス中の

不純物を除去する目的で、アルミニウム電極2枚を610℃の溶融フラックス中に対向させ、電極間に直流2Vをかけ、電流値3Aで1時間直流電解した（電極単位面積当り0.05A/cm²）。

その後ろう付け作業をしたところ、アルミニウムろう付け表面は光輝状態で接合された。

これは、溶融フラックス中の長時間の運転中に生じた微量の不純物である金属及び水分，酸素が除去されたためである。

実施例2

電気抵抗加熱によるニッケルーモリブデン合金のポットを用いて、実施例1と同一組成のフラックスを溶融し、同一条件でろう付けしたところ、良好な接合が得られた。

長時間運転後、ろう付け時にアルミニウム表面に黒色付着物が増加した。

そこで、運転を止め、実施例1と同様にフラックスを直流電解した。

その結果、アルミニウムろう付け部材の表面には光輝状態で接合された。

（ホ）発明の効果

本発明は上記のように$BaCl_2$，$NaCl$，$KCl$とフッ化物とでフラックスを用いたろう付け方法において、フラックスを常時清浄に保つことができ、アルミニウム又はその合金のろう付け性に必要な化学活性や溶融ろうとの置換性、ろう材に対応するフラックスの融点などを満足しながら、従来のフラックスによる浸漬ろう付けでの脱水作業のほとんどを省略することができ、また炉底部の沈殿物除去の軽減や吸水によるフラックスの組成変化の減少など多くの優れた効果をあげることができる。

特に、フラックスが容易に清浄化できるので、アルミニウム被ろう付け部材はその表面が光輝状態でろう付けされる利点は卓越したところである。

本発明は以上の如く、信頼性の高いろう付け性を維持しつつ、作業性や経済性を大きく改善した浸漬ろう付け接合方法を提供することができるものである。

02-B-180-A L


(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 163 471 A2**


# (12) EUROPEAN PATENT APPLICATION


(21) Application number: 85303540.0

(51) Int. Cl.⁴: B 21 C 9/00

(22) Date of filing: 20.05.85

(30) Priority: 21.05.84 JP 102339/84
03.08.84 JP 164150/84

(43) Date of publication of application:
04.12.85 Bulletin 85/49

(84) Designated Contracting States:
DE FR GB



(71) Applicant: SUMITOMO METAL INDUSTRIES, LTD.
15, Kitahama 5-chome Higashi-ku
Osaka-shi, Osaka, 541(JP)

(72) Inventor: Hagita, Hyoji
3-1-15-505, Moritsune Kokuraminami-ku
Kitakyushu-shi Fukuoka-ken(JP)

(72) Inventor: Fukuda, Takashi
400-15, Minamikata Kokuraminami-ku
Kitakyushu-shi Fukuoka-ken(JP)

(72) Inventor: Maeda, Shigeru
3-84, Ippongimachi
Handa-shi Aichi-ken(JP)

(72) Inventor: Imamura, Hideo
5-15-10, Hiiragi-cho
Handa-shi Aichi-ken(JP)

(72) Inventor: Ogata, Kazutosi
2-2-15, Kamiike-cho
Handa-shi Aichi-ken(JP)

(72) Inventor: Fukuoka, Masahiro
1-1, Higashihachigaike Miyoshi-cho
Nishikamo-gun Aichi-ken(JP)

(74) Representative: Baillie, Iain Cameron
c/o Ladas & Parry Isartorplatz 5
D-8000 München 2(DE)


## (54) Method for continuous drawing of wire rod.


(57) A wire rod is payed out from a pay-off stand and descaled in a descaling process. After preheating to a predetermined temperature by a preheating device, it is subjected to a lubrication pretreatment through a zinc calcium phosphate solution applied with ultrasonic wave in the lubrication pretreatment process. After rinsing process, the lubrication-pretreated wire rod is coated with a calcium stearate or a sodium stearate in lubricating process. Thereafter, the wire rod is dried sufficiently in drying process, and then added with a predies lubricant in wire drawing process and coiled by a coiler.



EP 0 163 471 A2

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BNSDOCID: <EP_________0163471A2_I_>

# METHOD FOR CONTINUOUS DRAWING OF WIRE ROD

The present invention relates to a method for continuous drawing of a wire rod for cold-forging, in which the wire rod (inclusive of a steel bar) is descaled, pretreated for lubrication, lubricated and drawn into wire while being moved continuously.

Secondary working for a wire rod for cold-forging is performed normally in the order: descaling (pickling) - lubrication pretreatment - lubrication - drying - wire drawing - coiling. Among them, pickling, lubrication pretreatment and lubrication are usually rendered in batch treatment system. That is, heretofore, a pickled wire rod coil was dipped in a phosphate solution of, for example, zinc phosphate and, thereafter, dipped in a lubricate solution of, for example, sodium stearate to form a lubricate coating of such materials as sodium stearate, zinc stearate, or zinc phosphate on the surface of the wire rod. The batch treatment system was heretofore used for the reason that a long period of reaction was required to obtain a coating having a thickness sufficient to provide satisfactory lubricating properties, this required a longer treatment time and made an in-line system difficult.

Therefore, in, for example, Japanese Patent Public Disclosure No. 163047/1981 Official Gazette, there is proposed a method for performing lubrication pretreatment and lubrication in an in-line system to thereby reduce equipment cost and improve productivity. This prior art method has been put into practical use. This prior art method is characterized in that, after descaling, a wire rod is coated with zinc phosphate (lubrication pretreatment), further coated thereon with calcium stearate at room temperature (lubrication), and then rapidly dried. In this prior art method, it is made possible to reduce running cost, to coat a required quantity of lubricant in a very short time, to dry it in a short time, and to make it in an in-line system without extending the entire line unduly.

According to prior art methods, however, any of the

batch treatment system or the in-line system used zinc phosphate solution as the lubrication pretreatment, and therefore, had a disadvantage that the lubricant coating had unsatisfactory resistance to heat.

Generally in metal wire drawing operation, as described above, lubricant is indispensable to improve the working efficiency, to prolong the tool life, and to maintain the surface quality of drawn wire.

The lubricant for wire drawing reduces the friction between the dies and the wire rod to thereby make it possible to draw the wire rod with a smaller drawing force and prevents wear of the dies. In addition to these functions, the lubricant has important advantage that it remains securely as a coating on the surface of the wire after drawing and acts as an effective lubricant during cold forming (for example, bolt making).

Heretofore, a predies lubricant having metallic soap as the main component as follows was normally used in drawing wire:

| | |
|---|---|
| metallic soap: | 60 - 80% (by weight) |
| inorganic material: | 20 - 40% (by weight) |
| additives: | several % (by weight) |

In the prior art lubricant for wire drawing having metallic soap as the main component in which the metallic soap displays the basic lubricating properties, stearate or palmitinate of alkali earth metals or sodium were normally used. The typical inorganic material used in the prior art wire drawing lubricant is lime which prevents temperature rise in heavy working to thereby prevent adhesion between the wire rod and the dies and to control the softening temperature of the lubricant. The additives used in the prior art were one or more of sulfur, molybdenum disulfide and graphite which were added to prevent adhesion between the wire rod and dies under severe wire drawing conditions and to improve the lubricating properties.

However, while the prior art wire drawing lubricant having metallic soap as the main component had better properties than other wet type lubricants, it was still

insufficient in the lubricating properties such as resistance to heat produced in drawing and adhesiveness of the lubricant coating formed, which made the life of the wire drawing dies and the life of the dies for cold-forging subsequent to drawing relatively short.

The drawn wire rods are mostly cold-forged into products. However, it has become a recent trend that the lubricant used in the wire drawing is left adhering onto the surface of the wire brought to the cold-forging process so that the wire can be cold-forged into products without adding any lubricant. Therefore, while much better adhesiveness after wire drawing and higher heat-resistance sufficient to prevent cracking in the adhering lubricant coating after wire drawing have been demanded for the lubricant for wire drawing, no successful lubricant for wire drawing which satisfactorily answer to these demands has been found yet.

An object of the present invention is to provide a method for continuous drawing of wire rod, in which the wire rod is descaled, pretreated for lubrication, lubricated, dried and drawn into wire in an in-line system to thereby make it possible to obtain a lubricant coating highly resistant to heat and to carry out the wire drawing operation efficiently in a shorter period of time than prior art methods.

Another object of the present invention is to provide a lubricant for wire drawing, which is capable of overcoming the above-described problems of the prior art lubricants and has highly desirable properties such as reduction in friction, resistance to heat, and deposition and adherence to the wire rod, to thereby prolong the life of the dies for wire drawing and cold-forging.

The continuous wire drawing method according to the present invention is characterized in that a descaled and preheated wire rod is pretreated for lubrication by passing it through a calcium zinc phosphate solution (Ca/Zn = 0.3 - 1.0) maintained in the temperature range 70°C - 90°C and added with an ultrasonic wave (frequency: 10 - 60 KHZ,

output: 25 W/1 litre solution), rinsed, lubricated by causing calcium stearate to adhere to it at room temperature or passing it through a sodium stearate solution maintained in the temperature range 70°C - 90°C, dried and then drawn into wire. Further, in said wire drawing operation, the predies lubricant having metallic soap as the main component added with 1 - 10 weight % of a thermoplastic resin (for example, Teflon, polyethylene, nylon, acrylic resin, polycarbonate) is used.

We have discovered that in wire drawing operation addition of a thermoplastic resin to the prior art predies lubricant having metallic soap as the main component improves the lubricating properties of the lubricant considerably. That is, by adding 1 - 10% by weight of a thermoplastic resin to the prior art predies lubricant having metallic soap as the main component, the lubricating properties of the lubricant, such as reduction of friction and resistance to heat, can be greatly improved.

Addition of the thermoplastic resin in less than 1% by weight is insufficient to improve the lubricating properties satisfactorily. On the other hand, addition of it in more than 10% by weight increases the cost unduly and may result in generation of thermally decomposing gases during heat treatment after cold-forging. Particularly when any of fluorine-contained polymers is used, addition of it in a percentage higher than specified above is accompanied by the risk of generation of fluoric gas during heat treatment after cold-forging. Accordingly, great care must be taken in determination of the percentage of addition of the thermoplastic resin.

The term "metallic soap" as used herein is to be understood to mean metallic salts other than alkali salt, of, such as, fatty acid, resin acid and naphthenic acid, inclusive of sodium salt of these acids and their mixtures, preferably of common composition (commonly used as wire drawing lubricant) containing calcium stearate or sodium stearate in 90% or more in weight added with one or more of aluminum stearate, zinc stearate and barium stearate in

several percent by weight.

Further, the term "a predies lubricant having metallic soap as the main component" as used herein is to be understood to mean any of lubricants containing said metallic soap in 60% or more by weight, inorganic material (such as lime) in 20% or more by weight, and several percent of additives (one or more of sulfur, molybdenum disulfide and graphite), that is, this term is applicable to any of known wire drawing lubricants.

The term "thermoplastic resin" as used herein is to be understood to apply to any of polyethylene resin, polypropylene resin, fluorine-contained polymers known as Teflon (trademark), polystyrene resin, vinyl acetal resin, polyacrylate resin, polymethacrylate resin, polyvinyl chloride resin, polyvinylidene chloride resin, polyacrylonitrile resin, polyvinylether resin, polyvinylketone resin, polyether resin, polycarbonate resin, thermoplastic polyester resin, polyamide resin, diene resin, polyurethane resin, and silicone resin. These resins are used solely or in combination of two or more kinds of them.

The thermoplastic resin is added preferably in the form of powder of the size approximately of 10 - 20 μm diameter.

The invention will be better understood from the following description taken in connection with the accompanying drawings in which:

Fig. 1 is a block diagram of the process of the method for continuous drawing of wire rod according to the present invention;

Fig. 2 is a graph showing the effect of application of an ultrasonic wave to lubrication pretreatment in the present invention;

Fig. 3 is a graph showing the relationship between the frequency of the ultrasonic wave and the zinc calcium phosphate coating weight;

Fig. 4 is a graph showing the relationship between Ca/Zn ratio of the calcium zinc phosphate coating and the

zinc calcium phosphate coating weight;

Fig. 5 is a graph showing the relationship between the concentration of calcium stearate and the calcium stearate coating weight;

Fig. 6 is a graph showing the relationship between the treating time of the sodium stearate and the zinc stearate coating weight;

Fig. 7 is a schematic side view of an apparatus for ultrasonic pretreatment for lubrication;

Fig. 8 is a schematic front view of a treating bath;

Fig. 9 is a graph showing the relationship between the quantity of ethylene tetrafluoride resin added to the predies lubricant having metallic soap as the main component and the drawing force in the wire drawing operation using the lubricant;

Fig. 10 is a graph showing the adhesiveness of the lubricant coating in the cold-forging process;

Fig. 11a is a schematic view of the shape of the cut wire rod before cold-forging;

Fig. 11b is a schematic view of the shape of the product of the cold-forging;

Fig. 12 is a graph showing comparatively the results of Bowden tests of the materials subjected to wire drawing and cold-forging using the lubricant according to the present invention and the conventional lubricant, respectively; and

Fig. 13 is a graph showing the results of Bowden tests of the material in an example of the present invention.

With reference now to the drawings and more particularly to Fig. 1 thereof, there is shown in block diagram treating processes of the method according to the present invention. As shown, a wire bar is payed out from a pay-off stand 1 and descaled in descaling process 2 by, for example, shot blasting. Subsequently, the wire rod is preheated by a preheating device 3 to a predetermined temperature (80°C or higher) and then pretreated for lubrication in lubrication pretreatment process 4 by passing it through a calcium zinc phosphate solution (Ca/Zn = 0.3 - 1.0) added with an

ultrasonic wave. The calcium zinc phosphate solution is preheated to the temperature 70 - 90°C. Then, after rinsing process 5, the pretreated wire rod is lubricated by calcium stearate or sodium stearate to adhere thereto in lubricating process 6. Lubrication by calcium stearate is carried out at room temperature. However, sodium stearate is to be preheated to 70 - 90°C for lubrication in process 6. After lubricated, the wire rod is dried sufficiently in its lubricant coating in drying process 7, drawn with a predies lubricant in wire drawing process 8, and coiled by coiler 9.

Method of descaling rod used in descaling process 2 is not limited. Any of pickling, shot blasting and roll bending may be used to descale the rod in process 2. Among the three methods mentioned above, shot blasing is most preferable for the phosphate coating in an in-line system.

The method according to the present invention is characterized in that calcium zinc phosphate (Ca/Zn = 0.3 - 1.0) having a good resistance to heat is used in process 4 to pretreat the wire rod for lubrication. The temperature of removing crystal water of the calcium zinc phosphate coating is 415°C while the temperature of removing crystal water of the heretofore used zinc phosphate coating is 280 - 290°C. This means that the prior art zinc phosphate coating is removed of its crystal water by the heat (normally up to 300°C) developed during wire drawing operation to thereby cause cracks in the coating. In contrast to this, since the temperature of removing crystal water of the calcium zinc phosphate coating according to the present invention is, as mentioned above, as high as 415°C, no crack is caused in the coating by the wire drawing operation.

The method according to the present invention is characterized in that an ultrasonic wave is used in treatment to obtain a sufficient zinc calcium phosphate coating weight and to control the coating weight. This is because the calcium zinc phosphite solution is less sensitive to chemical conversion treatment than the zinc phosphate solution and is more difficult to obtain the coating weight. However, as shown in Fig. 2, the zinc calcium phosphate coating weight

is increased by application of the ultrasonic wave thereto. The results shown in Fig. 2 were obtained under the treatment conditions: concentration 160 points, temperature 80°C, and frequency of the ultrasonic wave 50 KHZ at 1 KW.

As shown in Fig. 3, the frequency of the ultrasonic wave applied to the solution is preferably in the range 10 - 60 KHZ because the frequency lower than 10 KHZ presents a problem of noise and, on the other hand, the frequency higher than 60 KHZ is less effective to obtain a sufficient coating weight. Output of the ultrasonic wave is preferably 25 W per litre of the solution.

The Ca/Zn ratio of the calcium zinc phosphate coating is determined to 0.3 - 1.0 for the reason described below. Fig. 4 shows the relationship between the Ca/Zn ratio of the calcium zinc phosphate coating (concentration of the solution 160 points) and the coating weight. As understood from Fig. 4, when the Ca/Zn ratio is lower than 0.3, effect of addition of Ca is small and the resistance to heat is not sufficient. On the other hand, when the Ca/Zn ratio is higher than 1.0, the sensitiveness to chemical conversion treatment is not sufficient and it is difficult to obtain a predetermined coating weights ($\geq 6$ g/m$^2$) and of metallic soap ($\geq 1$ g/m$^2$). Accordingly, the Ca/Zn ratio of the calcium zinc coating is preferably in the range 0.3 - 1.0.

The predetermined coating weight of the calcium zinc phosphate coating weight of 6 g/m$^2$ or larger is obtained in a short period of time 10 - 20 seconds only when the concentration of the calcium zinc phosphate solution is 160 points or higher. On the other hand, the concentration of the solution of 200 points or higher is not ecomonical since the coating weight in proportion to the increase in the concentration is not obtained. Here, the lower limit of the coating weight of the calcium zinc phosphate coating is predetermined to 6 g/m$^2$. The prior art zinc phosphate coating having lower resistance to heat requires the coating weight of the lower limit 7 - 8 g/m$^2$. However, since the calcium zinc phosphate coating according to the present invention has a high resistance to heat, the coating weight of it can

satisfactorily be as low as 6 $g/m^2$.

The apparatus used for ultrasonic pretreatment for lubrication in the method according to the present invention may take the construction in which, as shown in Figs. 7 and 8, a plurality of ultrasonic wave applying devices 12 are disposed vertically or horizontally in pairs in parallel or staggered positions on the outer peripheral surface of a cylindrical treating bath 11, return pipes 14 are provided between treating solution receivers 13 projecting from the inlet side and the outlet side, respectively, of the treating bath 11 and a treating solution tank 15 to collect treating solution 19 therethrough, and a pump 16 is provided to supply the treating solution from the treating solution tank 15 to the treating bath 11 through piping 17. By the apparatus constructed as described above, the calcium zinc phosphate solution is subjected to the ultrasonic wave and agitated, and caused to rapidly adhere to the surface of a wire rod 18 by cavitation. Further, it is made possible to control the coating weight of the calcium zinc phosphate solution by using or not using the application of the ultrasonic wave or by changing the frequency or the output of the ultrasonic wave applying device.

The lubrication process is carried out after the lubrication pretreatment process by passing the wire rod either (1) through calcium stearate solution at room temperature or (2) through sodium stearate solution heated to the temperature 70 - 90°C.

In lubrication with calcium stearate (1), as will be understood from the relationship between the concentration and the coating weight shown in Fig. 5, the concentration must be 300 g/litre or higher in order to obtain the predetermined coating weight of 5 $g/m^2$ or higher. While any of wet spraying (coating solution) and dry spraying (coating powder) can be used to cause calcium stearate to adhere to the wire rod, coating by wet spraying is preferred in view of the coating weight of the lubricant and the adhesiveness of the lubricant coating. Treating time of 2 - 3 seconds is normally required for physical adhesion.

In lubrication with sodium stearate (2), batch treatment system can be used. In this lubrication with sodium stearate, substitution takes place between the calcium zinc phosphate coating formed by lubrication pretreatment and the sodium stearate solution to produce a zinc stearate layer which adheres to the surface of the wire rod. In this lubrication, it is normally required to obtain the coating weight of the substitution product layer of 1 $g/m^2$ or higher. For this purpose, as seen from the relationship between the treating time with sodium stearate and the zinc stearate coating weight shown in Fig. 6, a period of time of 20 seconds or longer is required.

The lubrication (1) or (2) above may be omitted in the case where a predies lubricant is used during wire drawing process.

In the method according to the present invention, the predies lubricant is added to increase the heat-resistance and lubricating properties. The predies lubricant used in the method according to the present invention is the lubricant having metallic soap as the main component added with a thermoplastic resin such as Teflon, polyethylene, nylon, acrilic resin, and polycarbonate in 1 - 10% by weight. The thermoplastic resin is added to the metallic soap lubricant to make use of the heat-resistance and the low friction of the thermoplastic resin such, for example, as Teflon. Further, the quantity of addition of the thermoplastic resin is determined to 1 - 10% by weight because addition of it in less than 1% is not sufficient to provide an effect to the drawing force and, on the other hand, while a larger quantity of addition of it provides a larger effect, the upper limit of the quantity of its addition is determined to 10% considering the cost and the fact that the decomposition gas of, for example, Teflon is fluorine gas.

Fig. 9 shows graphically the relationship between the quantity of addition of ethylene tetrafluoride (trademark "Teflon") to the wire drawing lubricant containing metallic soap as the main component (having the content: calcium stearate 70%, lime 27%, and sulfur 3% by weight) and the

drawing force required to draw a steel rod (equivalent to S45C of JIS - Japanese Industrial Standard) into wire. The graph of Fig. 9 shows the results of drawing of said steel rod coated with zinc phosphate as the lubrication pretreatment and having the diameter 5.5 mm$^{\phi}$ into wires with two different reduction of area, approximately 20% and approximately 30%, respectively.

It is clear from Fig. 9 that the required drawing force shows the tendency to decrease suddenly when the quantity of addition of the ethylene tetrafluoride containing resin exceeds 1% by weight. This tendency has been confirmed to appear likewise when other thermoplastic resin is added. While the graph of Fig. 9 shows that the thermoplastic resin is added preferably in larger quantity from the view to increase the lubrication, the quantity of its addition is required to be limited to 10% by weight or less in view of the environmental pollution and economy as mentioned hereinabove.

Fig. 10 shows graphically the comparative results of the adhesiveness of the lubricant coating to the rod being worked between the predies lubricant with no resin added and the predies lubricant with a thermoplastic resin added.

The wire drawing lubricant, the thermoplastic resin added and the lubrication pretreatment method used in the tests shown in Fig. 10 were the same as those used in the tests of Fig. 9, and the wire rod used was a boron steel equivalent to 10B22M of AISI. The coating weight was measured in the manner described below.

A boron steel rod of the diameter 22 mm$^{\phi}$ coated with zinc phosphate or zinc calcium phosphate (pretreatment for lubrication) was drawn into rod of 19.5 mm$^{\phi}$ with the reduction of area of approximately 21.4% using both of the predies lubricant added with no resin and the predies lubricant added with ethylene tetrafluoride containing 3% by weight, and subjected to cold-forging (extruding to make bolts) during which sampling is started to find the rate of residual lubricant on the drawn rod (extruding reduction of area = 0) at each extruding reduction of area. That is, the adhesiveness

of the lubricant coating is understood as the following ratio:

$$\frac{\text{coating weight after extrusion}}{\text{coating weight to mother material}}$$

The larger the value of the rate of residual lubricant coating is, the better the adhesiveness of the coating is or the more the lubricant remains and, accordingly, the less frequently the seizure occurs during the cold-forging operation. In the cold-forging used in the method according to the present invention, a rod (diameter: $d_0$) shown in Fig. 11a is formed to, as shown in Fig. 11b, a bolt-like shape (diameter of shank: $d_1$) leaving a head undrawn, with the ratio of maximum accumulated reduction of area of approximately 80%. In this case, the ratio of reduction of area is given by the formula:

$$[1 - (\frac{d_1}{d_0})^2] \times 100.$$

It is understood from the results shown in Fig. 10 that the predies lubricant added with ethylene tetrafluoride containing 3% by weight is obviously superior in adhesiveness of the lubricant coating to the lubricant added with no resin. This shows that the addition of the ethylene tetrafluoride increases the heat resistance of the lubricant and prevents its deterioration by heat generated during working.

Fig. 12 shows the results of Bowden tests (using a Bowden tester for rubbing the surface of the test piece by a steel ball to determine the coefficient of friction corresponding to the number of sliding times) using extruded rods obtained by the cold-forging process described above (extrusion reduction of area: approximately 79.5%).

It is understood from Fig. 12 that the rod coated thereon with the predies lubricant added with the ethylene tetrafluoride in 3% by weight has obviously lower coefficient of friction than the rod coated thereon with the predies lubricant added with no such resin and is lower in the rise of the coefficient of friction than it. Therefore, Fig. 12 shows that the predies lubricant added with the thermoplastic resin is superior in lubricating properties and adhesiveness of its coating.

**Example**

By the equipment having the line construction shown in Fig. 1, using shot blasting for descaling of the wire rod, and including the ultrasonic pretreatment apparatus for lubrication shown in Figs. 7 and 8, a material of 5.5 mm$^{\phi}$ (S45C) was drawn in the following operating conditions into rods of 4.95 mm$^{\phi}$ and 4.6mm$^{\phi}$, respectively:

Operating Conditions:

(1) Descaling Condition

Shot blasting Material: steel balls 0.3 mm$^{\phi}$

Shot Density: approximately 300 Kg/m$^2$

(2) Preheating Condition

Steam Blowing: at temperature of 80°C

(3) Lubrication Pretreatment Condition

Lubrication Pretreating Agent: calcium zinc phosphate solution (Ca/Zn = 0.5)

Treatment Condition: 160 points (concentration) x 80°C (temperature) x 15 sec. (reaction time), ultrasonic wave: 50 KHZ, 1 KW

(4) Lubricating Condition

(i) When using calcium stearate

Concentration: 300 g/litre

Temperature: room temperature

Time: 3 seconds

(ii) When using sodium stearate

Concentration: 90 g/litre

Temperature: 80°C

Time: 25 seconds

(5) Drying Condition

Infrared Drying Furnace: furnace temperature 80°C

(6) Wire Drawing Condition

Predies Lubricant: lubricant having calcium stearate as the main component added with Teflon in 3%

Reduction of Area:

approximately 19% (5.5 mm$^{\phi}$ → 4.95 mm$^{\phi}$)

approximately 30% (5.5 mm$^{\phi}$ → 4.6 mm$^{\phi}$)

Wire Drawing Speed: 80 m/mm

Table 1 shows the drawing force in the method according to the present invention in comparison with prior art method (Lubrication Pretreatment: zinc phosphate, Predies Lubrication: only a lubricant on the market having calcium stearate as the main component).

Table 1 : Drawing Force

| Lubricating Condition \ Ratio of Drawing Reduction of Area (%) | | | $5.5^{\phi} \rightarrow 4.95^{\phi}$ (approx. 19%) | $5.5^{\phi} \rightarrow 4.6^{\phi}$ (approx. 30%) |
|---|---|---|---|---|
| Present Invention | 1 | calcium zinc phosphating — predies lubrication added with Teflon | 785 Kg. | 970 Kg |
| Present Invention | 2 | calcium zinc phosphating — calcium stearate + predies lubrication added with Teflon | 770 Kg | 950 Kg |
| Present Invention | 3 | calcium zinc phosphating — sodium stearate + predies lubrication added with Teflon | 730 Kg | 910 Kg |
| Prior Art | | zinc phosphating — calcium stearate predies lubrication | 822.5 Kg | 1032.5 Kg. |

Fig. 10 shows the results of Bowden tests (lubricating properties and adhesiveness of the lubricant coating) of the rod after winding. Table 2 shows the number of sliding times when $\mu = 0.2$ in comparison between the method according to the present invention and the prior art method.

Table 2 : Bowden Slidng Times ($\mu$=0.2)

| Ratio of Reduction of Area | | $5.5^{\phi} \rightarrow 4.95^{\phi}$ | $5.5^{\phi} \rightarrow 4.6^{\phi}$ |
|---|---|---|---|
| Present Invention | 1 | 300 | 215 |
| Present Invention | 2 | 330 | 240 |
| Present Invention | 3 | 365 | 270 |
| Prior Art | | 92 | 74 |

Table 3 shows the life of each of the wire drawing dies and the cold-forging dies used for drawing rods under the conditions described above (provided, the drawing reduction of area: $5.5^{\phi} \rightarrow 4.95^{\phi}$) and then cold-forging them into high tension bolt in comparison with such life in the prior art.

Table 3 : Life of Wire Drawing and Cold-Forging Dies

| | Wire Drawing Dies | Cold-Forging Dies |
|---|---|---|
| Present Invention | 50 tons | 800 tons |
| Prior Art | 10 tons | 240 tons |

Life is expressed by tons of products before replacement of the dies for wear or damage thereof.

As will be seen from Tables 1 and 2 and Fig. 13, the lubricant coating according to the present invention is superior in heat resistance and adhesiveness to the zinc phosphate coating according to the prior art. Accordingly, the life of the drawing and the cold forging dies is considerably prolonged in the method according to the present invention.

In the method according to the present invention, as described hereinabove, since calcium zinc phosphate is used as the lubrication pretreating agent, it is made possible to obtain a coating having a higher temperature of removing crystal water and a higher heat resistance than the zinc phosphate coating according to the prior art, and since an ultrasonic wave applying device is used, it is made possible to secure and control freely coating weight of the calcium zinc phosphate coating. Further, since the lubricant pretreated rod is lubricated by calcium stearate or dodium stearate, the lubricating properties as well as the heat resistance can be improved. Moreover, since a prior art lubricant having metallic soap as the main component added with a thermoplastic resin such as Teflon is used as the predies lubricant during wire drawing operation, it is made

possible to improve the heat resistance and the lubricating properties of the lubricant coating and to prolong considerably the life of the cold-working tools.

While we have described and illustrated a present preferred method of practicing the invention, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously practiced within the scope of the following claims.

We claim:

1. A method for continuous drawing of a wire rod, in which the wire rod is descaled, pretreated for lubrication, lubricated, and drawn into wire while being moved continuously, said method comprising the processes of:

pretreating, after descaling, a preheated wire rod for lubrication, by passing it through a calcium zinc phosphate solution heated to 70 - 90°C;

lubricating, after rinsing said pretreated wire rod by coating it with a calcium stearate or a sodium stearate; and

drawing, after drying, said lubricated wire rod into wire.

2. A method according to Claim 1, characterized in that an ultrasonic wave is applied to said calcium zinc phosphate solution in said process of pretreatment for lubrication.

3. A method according to Calim 2, characterized in that the ultrasonic wave applied to said calcium zinc phosphate solution has the frequency of 10 - 60 KHZ and the output of 25 W/1 litre solution.

4. A method according to Claim 1, characterized in that said calcium zinc phosphate solution has the ratio (Ca/Zn) = 0.3 - 1.0.

5. A method according to Claim 1, characterized in that, in said lubricating process, said pretreated wire rod is coated with a calcium stearate at room temperature.

6. A method according to Claim 1, characterized in that said pretreated wire rod is passed through a sodium stearate solution heated to 70 - 90°C to coat it with said solution.

7. A method according to Claim 1, characterized in that, in said process for drawing wire after drying, a wire drawing lubricant having metallic soap as the main component added with a thermoplastic resin in 1 - 10% by weight is used as the predies lubricant.

FIG. 1

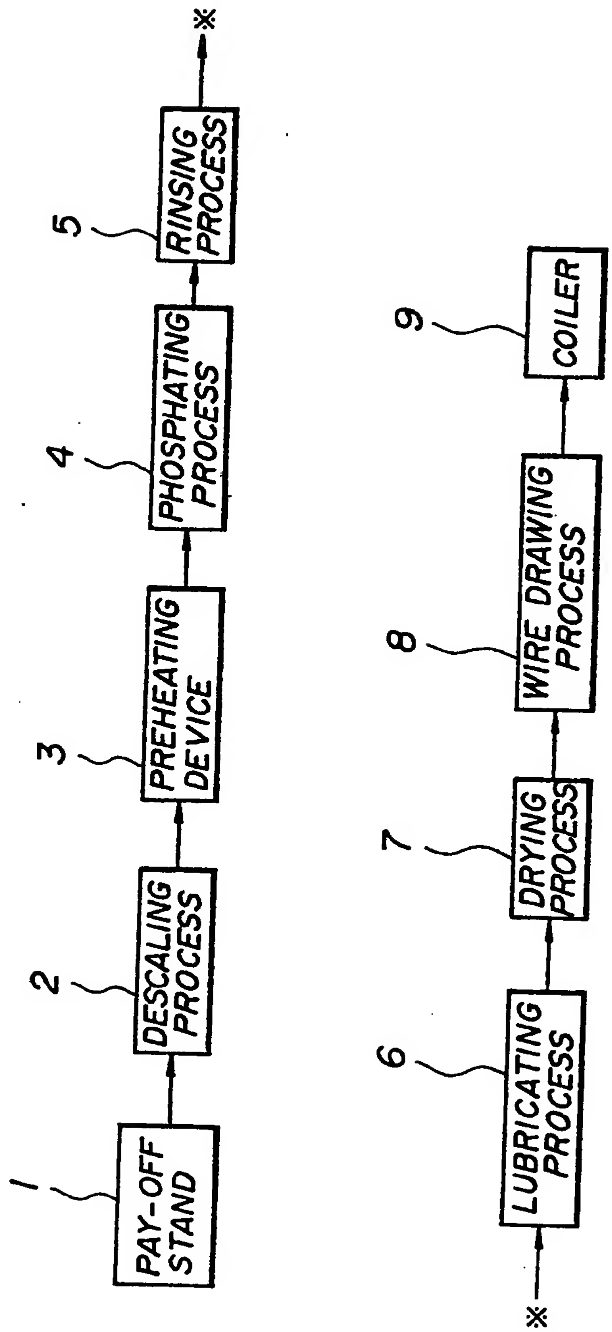

1
PAY-OFF STAND
2
DESCALING PROCESS
3
PREHEATING DEVICE
4
PHOSPHATING PROCESS
5
RINSING PROCESS
※
※
6
LUBRICATING PROCESS
7
DRYING PROCESS
8
WIRE DRAWING PROCESS
9
COILER

FIG. 2

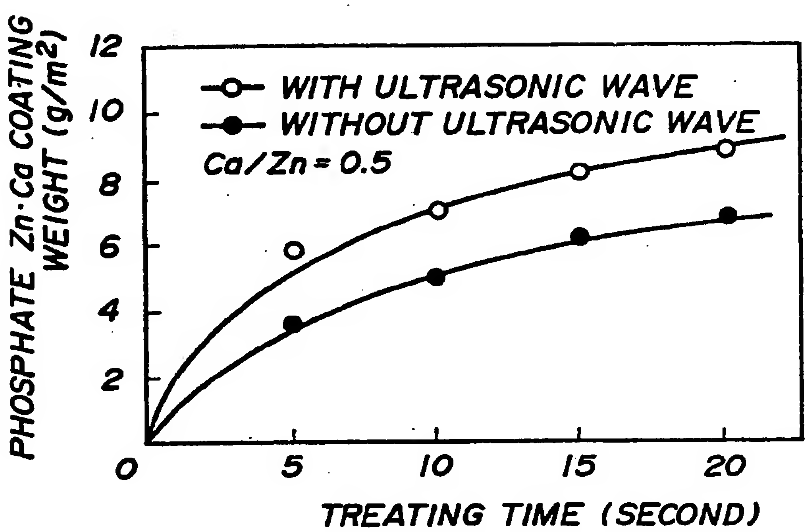

12
10
8
6
4
2
0
5
10
15
20
PHOSPHATE Zn·Ca COATING WEIGHT (g/m²)
TREATING TIME (SECOND)
WITH ULTRASONIC WAVE
WITHOUT ULTRASONIC WAVE
Ca/Zn = 0.5

FIG. 3

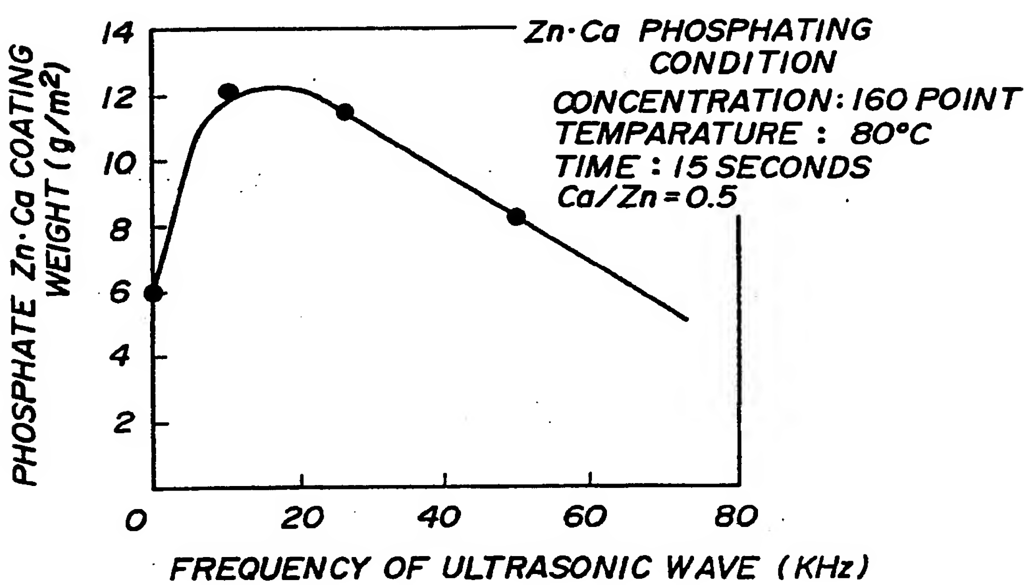

14
12
10
8
6
4
2
0
20
40
60
80
PHOSPHATE Zn·Ca COATING WEIGHT (g/m²)
FREQUENCY OF ULTRASONIC WAVE (KHz)
Zn·Ca PHOSPHATING CONDITION
CONCENTRATION: 160 POINT
TEMPARATURE : 80°C
TIME : 15 SECONDS
Ca/Zn = 0.5

FIG. 4

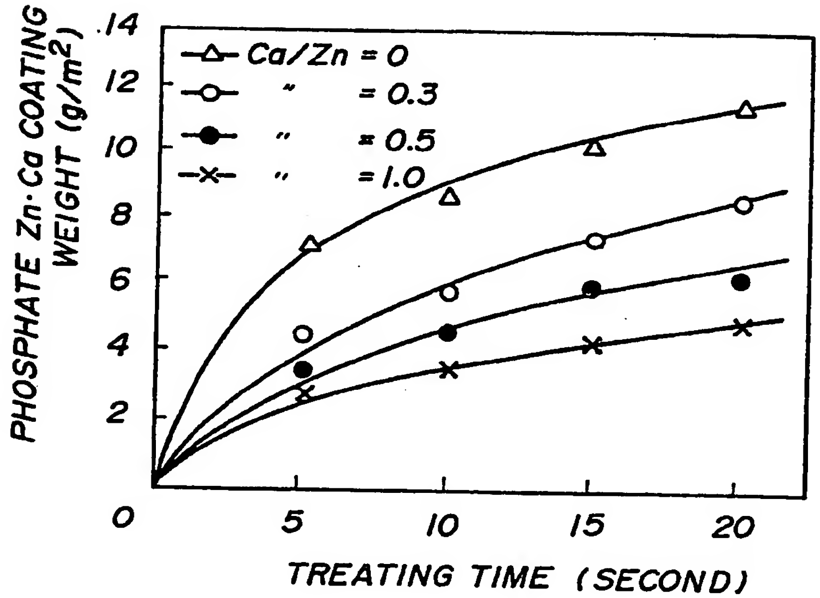

PHOSPHATE Zn·Ca COATING WEIGHT (g/m²)
14
12
10
8
6
4
2
0
Ca/Zn = 0
" = 0.3
" = 0.5
" = 1.0
5
10
15
20
TREATING TIME (SECOND)

FIG. 5

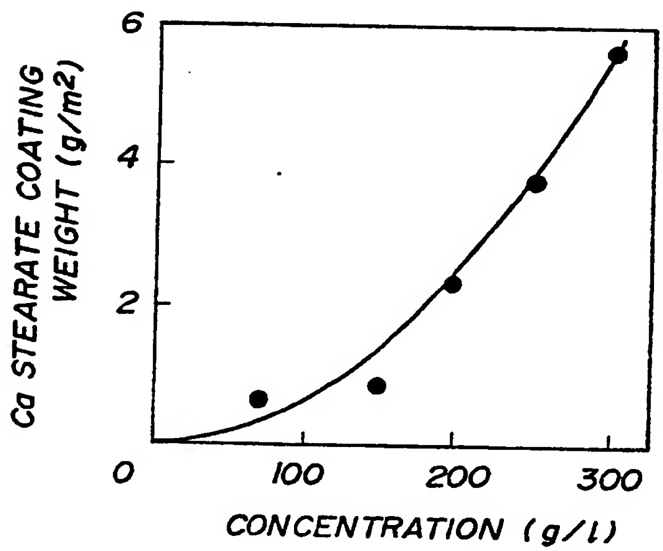

Ca STEARATE COATING WEIGHT (g/m²)
6
4
2
0
100
200
300
CONCENTRATION (g/l)

FIG. 6

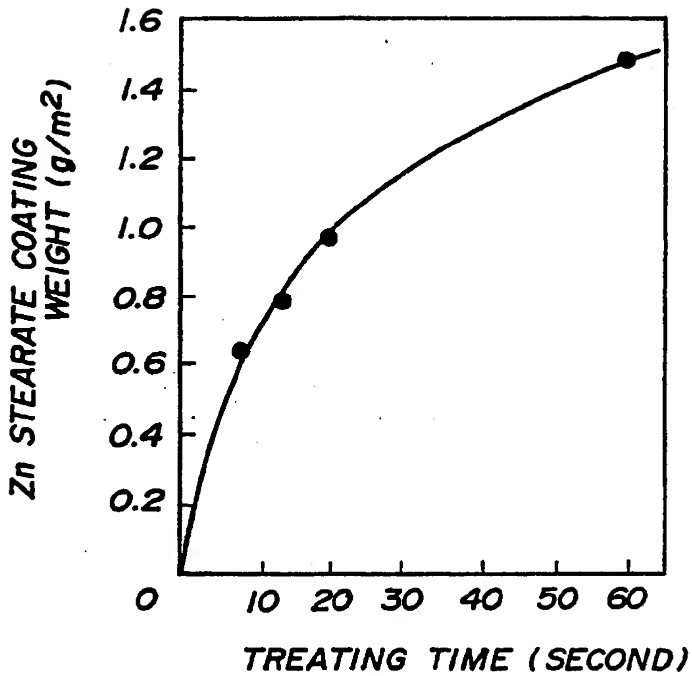

Zn STEARATE COATING WEIGHT (g/m2)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
50
60
TREATING TIME (SECOND)

FIG. 7

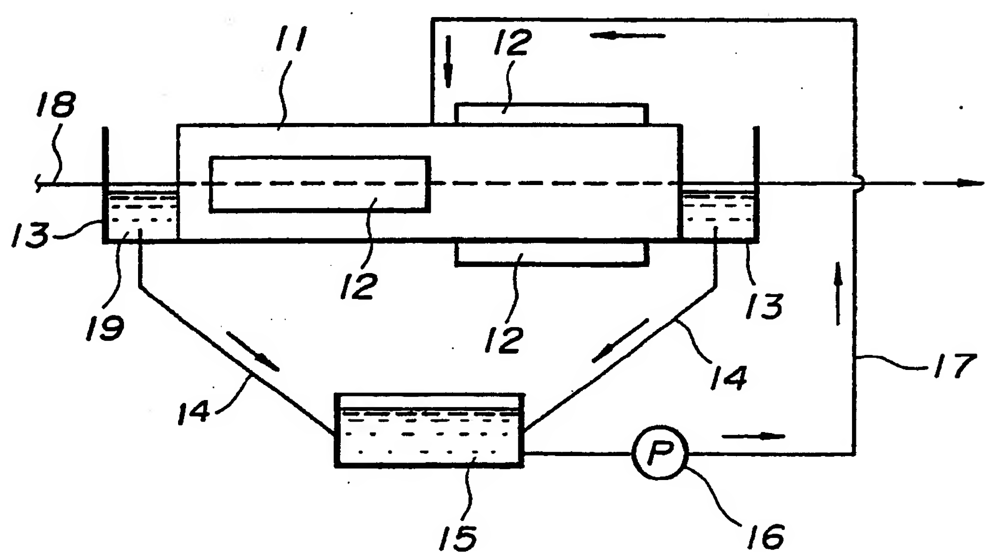

11
12
18
13
12
12
13
19
14
14
17
P
15
16

FIG.8

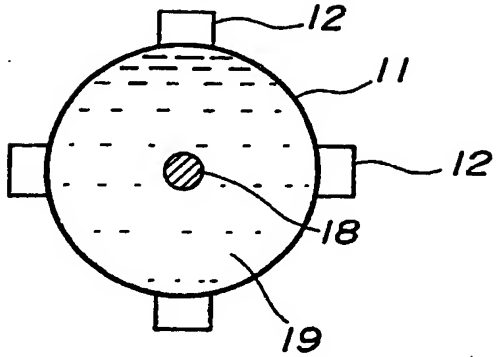

12
11
12
18
19

FIG.9

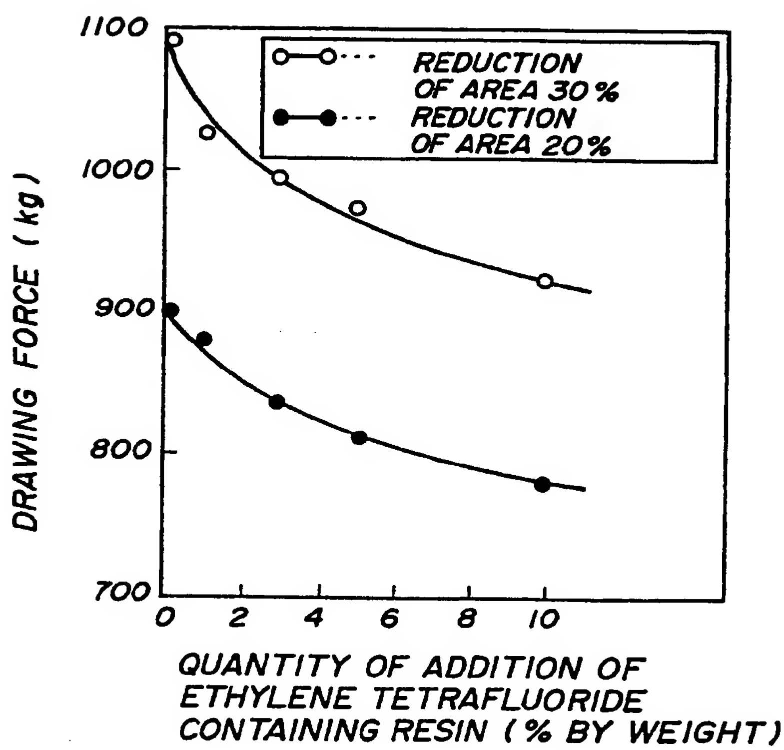

1100
1000
900
800
700
DRAWING FORCE (kg)
REDUCTION OF AREA 30%
REDUCTION OF AREA 20%
0
2
4
6
8
10
QUANTITY OF ADDITION OF ETHYLENE TETRAFLUORIDE CONTAINING RESIN (% BY WEIGHT)

FIG. 10

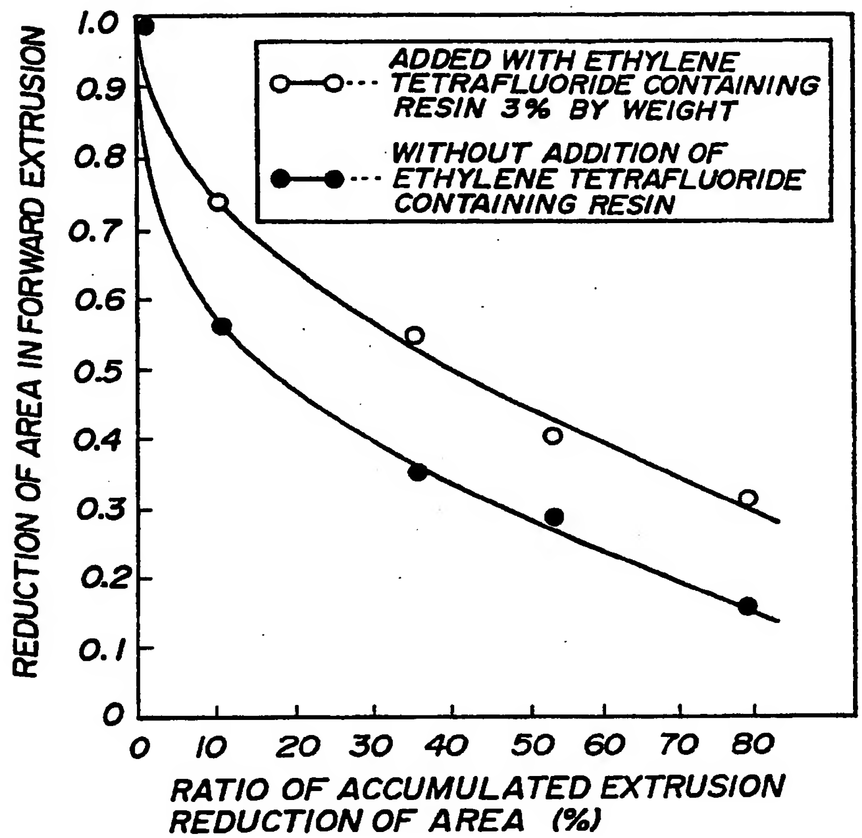



FIG. 11(a) FIG. 11(b)

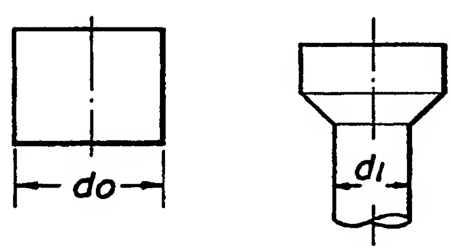


FIG. 12

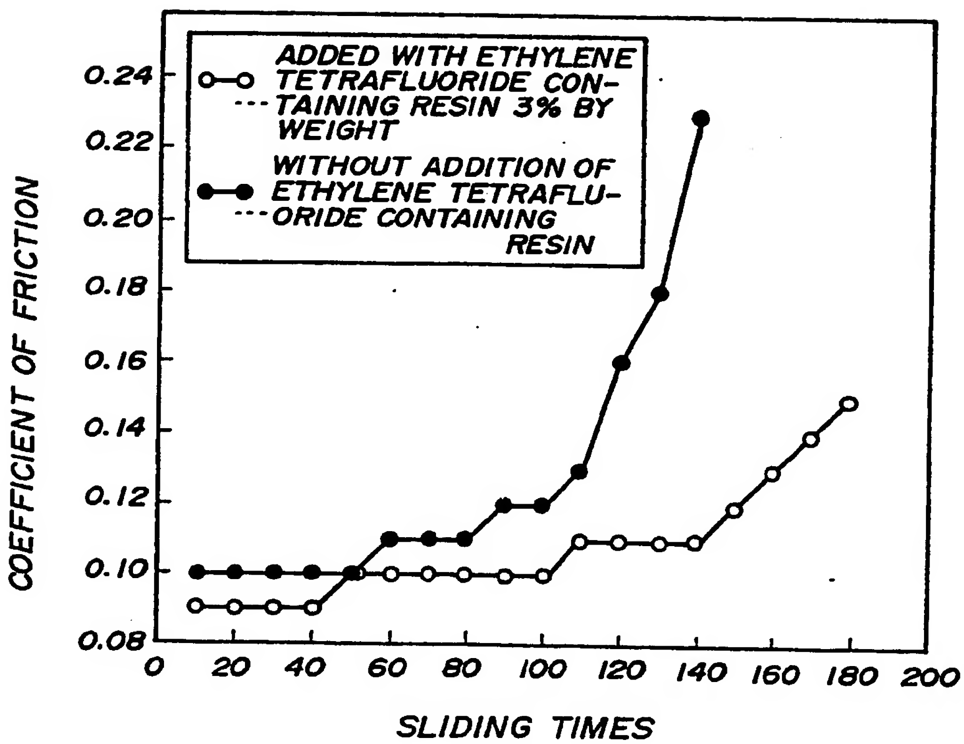
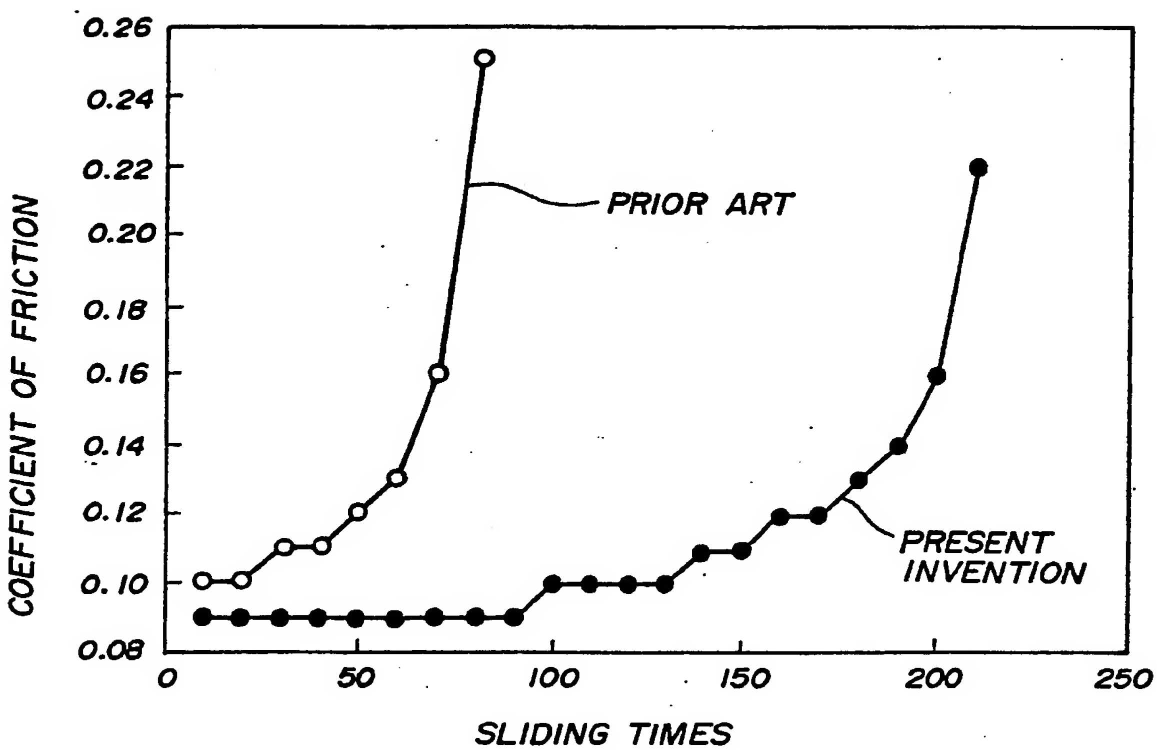

ADDED WITH ETHYLENE TETRAFLUORIDE CONTAINING RESIN 3% BY WEIGHT
WITHOUT ADDITION OF ETHYLENE TETRAFLUORIDE CONTAINING RESIN
COEFFICIENT OF FRICTION
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0
20
40
60
80
100
120
140
160
180
200
SLIDING TIMES

FIG. 13


COEFFICIENT OF FRICTION
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0
50
100
150
200
250
SLIDING TIMES
PRIOR ART
PRESENT INVENTION

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 163 471 A3

# (12) EUROPEAN PATENT APPLICATION

(21) Application number: 85303540.0

(22) Date of filing: 20.05.85

(51) Int. Cl.⁴: B 21 C 9/00

(30) Priority: 21.05.84 JP 102339/84
03.08.84 JP 164150/84

(43) Date of publication of application: 04.12.85
Bulletin 85/49

(84) Designated Contracting States: DE FR GB

(88) Date of deferred publication of search report: 18.06.86 Bulletin 86/25

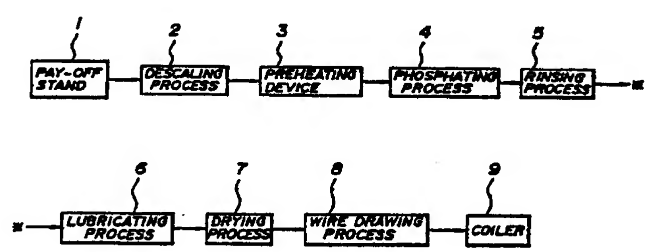
(71) Applicant: SUMITOMO METAL INDUSTRIES, LTD., 15, Kitahama 5-chome Higashi-ku, Osaka-shi, Osaka, 541 (JP)

(72) Inventor: Hagita, Hyoji, 3-1-15-505, Moritsune Kokuraminami-ku, Kitakyushu-shi Fukuoka-ken (JP)
Inventor: Fukuda, Takashi, 400-15, Minamikata Kokuraminami-ku, Kitakyushu-shi Fukuoka-ken (JP)
Inventor: Maeda, Shigeru, 3-84, Ippongimachi, Handa-shi Aichi-ken (JP)
Inventor: Imamura, Hideo, 5-15-10, Hiiragi-cho, Handa-shi Aichi-ken (JP)
Inventor: Ogata, Kazutosi, 2-2-15, Kamiike-cho, Handa-shi Aichi-ken (JP)
Inventor: Fukuoka, Masahiro, 1-1, Higashihachigaike Miyoshi-cho, Nishikamo-gun Aichi-ken (JP)

(74) Representative: Baillie, Iain Cameron, c/o Ladas & Parry Isartorplatz 5, D-8000 München 2 (DE)

## (54) Method for continuous drawing of wire rod.

(57) A wire rod is payed out from a pay-off stand and descaled in a descaling process. After preheating to a predetermined temperature by a preheating device, it is subjected to a lubrication pretreatment through a zinc calcium phosphate solution applied with ultrasonic wave in the lubrication pretreatment process. After rinsing process, the lubrication-pretreated wire rod is coated with a calcium stearate or a sodium stearate in lubricating process. Thereafter, the wire rod is dried sufficiently in drying process, and then added with a predies lubricant in wire drawing process and coiled by a coiler.




EP 0 163 471 A3

0163471

European Patent Office

# EUROPEAN SEARCH REPORT

Application number

EP 85 30 3540

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
|---|---|---|---|
| | | | B 21 C 9/00 |
| X | DE-B-1 103 108 (KLINGHOFFER)<br>* claims 1-4 *<br>--- | 1 | |
| X | DD-A- 204 420 (VEB WÄLZLAGER)<br>* claims 1, 2; page 2, line 13 *<br>--- | 1 | |
| A | DE-A-2 357 045 (GUTEHOFFNUNGSHÜTTE)<br>* claim 1 *<br>--- | 7 | |
| A | EP-A-0 053 636 (VEB THÄLMANN)<br>* claim 4 *<br>--- | 1 | |
| A | US-A-2 871 140 (GOSS)<br>* claim 1 *<br>----- | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.4) |
| | | | B 21 C 9/00 |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| BERLIN | 24-02-1986 | SCHLAITZ J |

**CATEGORY OF CITED DOCUMENTS**

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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O : non-written disclosure
P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document

EPO Form 1503 03 82

02-B-190-4 W

# PATENT SPECIFICATION

NO DRAWINGS

**863,098**

*Date of Application and filing Complete Specification: May 21, 1959.*

*No. 17401/59.*

*Complete Specification Published: March 15, 1961.*

**Index at acceptance:**—Class 82(2), U4(A : B : C : D : E2A : E2B : E3 : F1 : G1 : G2 : H1 : H2 : H3 : H4 : J : M1 : M2 : P), U5, U7(A : B : C : D : G : K).

**International Classification:**—C23f.

COMPLETE SPECIFICATION

## Improvements relating to the Coating of Metallic Surfaces

We, THE PYRENE COMPANY LIMITED, a British Company, of Great West Road, Brentford, Middlesex, do hereby declare the invention, (a communication from Parker Rust Proof Company, a Corporation organised under the laws of the State of Michigan, United States of America, of 2177 East Milwaukee Avenue, Detroit 11, Michigan, United States of America) for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the formation of protective coatings on metallic surfaces by treating them with an aqueous composition which interacts with the surface.

Hitherto such compositions, which are generally solutions of coating-forming ingredients, have been applied either by flooding the surface with the aqueous composition, for example by immersion or roller coating, or by spraying the composition on the surface. Each of these methods is still widely used, and each has a field of operation in which it represents the most economical and most satisfactory method of application. However, each of these methods has drawbacks. Thus while flooding methods are highly satisfactory where heavy coatings are desired they are relatively slow, while the spray method is faster but is not particularly suited for use in the production of heavy coatings.

In both the spray and immersion methods the draining of the solution from the surface gives rise to problems. Firstly, the draining solution tends to flow in small rivulents and to form more or less coating in the path of flow than on the balance of the surface. Secondly, where the draining solution leaves the surface it tends to form a bead, beneath which the thickness of the coating again differs from that over the main part of the surface. These non-uniformities in the coating cause difficulties both in painting and in otherwise using the coated surface.

Another problem which is common to both spray and immersion application methods is that the composition of the solution tends to change with continued use, and special steps have to be taken to maintain it at its optimum composition. For example, certain of the coating-forming chemicals in the coating solution may be used up faster than others; certain non-coating-forming ions may tend to increase to detrimental concentrations; the solution may undergo oxidation; and foreign ions may enter the solution from the surface being coated. Oxidation of a coating solution is particularly likely to occur when it is sprayed through the air.

These difficulties are overcome according to the invention by preheating the surface to be coated and applying the aqueous coating composition in the form of finely divided particles, the temperature of the surface and the size and quantity of the particles being so correlated that the particles dry substantially in the position where they first strike the surface. It should be noted that although the coating formed by the particles is dry, it may contain water of hydration. The conditions are preferably such that excess water is driven off substantially instantaneously on contact with the surface. By working in this way flow of the coating composition over the surface, and consequent formation of rivulets and beads, is avoided, and excess of the composition is not drained from the surface for re-use. Provided the particles are applied uniformly over the surface, the coating will also be uniform.

The thickness of the coating may be increased by applying further layers of the coating composition in the same way. At least the first layers of the coating will consist of or contain the products of interaction of the coating composition and the surface, but subsequent layers may consist wholly or largely of

solidified coating composition. In some cases these dried upper layers may include water-soluble components and a part of the coating may be removed by rinsing with water, and with certain combinations of metal and coating composition, the coating may be completely water-soluble. If necessary the coating is cured after application.

The process of the invention may be used to coat both bare metal surfaces and surfaces which already have an integral coating thereon. In the former case the coating composition must be capable of reacting with the metal itself, and in the latter case with the preformed integral coating on the metal. The metals that can be coated include all those that can be used to react with aqueous acidic or alkaline coating compositions, e.g. including iron, steel, zinc, copper, aluminium, magnesium, brass, bronze and stainless steel. Among the already-coated surfaces that may be further coated are phosphate-coated surfaces, which may for example be given a chromate rinse. Preheating a metal surface in air may also produce an adherent oxide film which may react with the coating composition.

The aqueous coating composition may be in any form which can be reduced to finely divided particles, but is preferably a dilute aqueous solution, dispersion or emulsion. In particular the coating composition may be an aqueous acidic coating-forming solution of zinc phosphates, manganese phosphates, iron phosphates, alkali metal phosphates, oxalic acid or oxalate, a mineral acid solution, an aqueous acidic solution containing ions capable of forming sulphide coatings, such as sulphide or sulphite ions, a dilute acidic rinse solution, e.g. a chromic acid or dichromate solution, with or without additional acids as modifying ingredients, used to rinse bare metal or previously chemically coated metallic surfaces, an amine phosphate coating solution, an acidic or alkaline metallic chromate solution to form finish coatings or rinse coatings over preliminarily formed metallic phosphate or similar coatings, or a dilute aqueous dispersion or emulsion of phosphate having lubricating properties, e.g. lauryl phosphate.

The present invention is particularly suitable for producing a chromium-containing coating on a bare or phosphate-coated metal surface by forming a film of an aqueous solution of a hexavalent chromium compound on the surface, the solutions also containing an organic polymeric or resinous material, and then drying the film on the surface, the organic material, which is preferably polyvinyl alcohol or polyacrylic acid, and the conditions of drying being such that an insoluble coating is formed. Coating compositions for forming such a chromium-containing coating are described in our Specifications Nos. 840,890 and 845,259.

A metal surface to be coated should be in the condition conventionally used in coating by spraying or immersion; no further special cleaning is required.

The surface being coated must be hot enough both for reaction to take place between it and the coating composition and also for excess water and other volatile constituents to be rapidly vapourised. The exact temperature required will therefore depend among other factors upon the nature of the metal and of the coating composition. It is well known, for example, that the temperatures at which different phosphate-coating solutions operate most efficiently may vary as much as 100°F. In general it is found that metal being coated should be so heated that the surface temperature is at least 135°F after the coating composition has been applied, and it may be as high as 800°F. The metal should not, however, be heated to such a temperature that its metallurgical properties, e.g. hardness and elasticity, are impaired. Initial temperatures between 175°F and 500°F have been found in most cases to be satisfactory. Heat will be lost by the metal both in raising the temperature of the coating composition applied to it and in vaporising excess water and other volatile matter, so that the temperature of the metal will tend to fall during the coating process. If, as will generally be the case, all the heat needed is supplied by preheating the metal before applying the coating composition, the metal must therefore be preheated above the desired final temperature to an extent that will, under given coating conditions, depend on the thickness of the metal. Thus thin metal articles will need to be preheated to a higher initial temperature than thick ones in order to maintain a suitable surface temperature throughout the coating process.

Less heat will of course need to be supplied by the metal if the coating composition is also preheated above room temperature, and it may be advantageous, particularly when the metal is thin, to continue heating the metal, for example by means of infra-red lamps or by electrical induction, during the application of the coating composition.

It may also be desirable to supply further heat after the coating has been applied in order to complete the reaction with the metal surface, particularly when the coating is thick, or to cure the coating if it is a film-forming type containing synthetic resinous ingredients. This extra heat may for example be supplied by conventional ovens or by infra-red or radiant lamps.

The rate of vaporisation of water from the coating composition will depend on the humidity of the atmosphere which envelops the surface being coated as well as the temperature. It is therefore desirable to provide an exhaust system to remove the water vapour and other vaporised constituents from the neighbourhood of the surface. This may enable

a lower temperature to be used. In no circumstances should the temperature in the neighbourhood of the surface be allowed to remain saturated with water vapour during the application of the coating, as this may slow down the evaporation of excess water so much that the particles are able to coalesce and run over the surface.

The aqueous coating composition is preferably converted to finely divided particles and applied to the surface by means of a suitable atomising gun, and both the size of the particles or droplets formed and the quantity of these particles applied to a given area of the surface to be coated must be correlated with the temperature of the metal to ensure that the particles do not have a chance to run before the excess water has evaporated. The particles may be applied over the whole surface by moving the atomising gun or other source of atomised particles relative to the surface or moving the surface relative to the source. The quantity of coating material per unit area of the surface being coated to obtain the most uniform coating depends both on the size of the particle and the speed of relative motion between the source of atomised particles and the surface to be coated. A uniform coating on the entire surface is most easily obtained when the particles are extremely fine and the relative motion is slow. Under these circumstances, as the minute particles hit the surface substantially all of them tend to remain in place, react with the underlying surface and lie immediately adjacent to each other without pyramiding to sufficient extent to become sufficiently liquid to flow during atomisation. As the particle size increases, in order to avoid coalescence sufficient to produce surface irregularities, it is necessary to increase the rate of relative motion between the source of the particles and the surface being coated. As this relative rate of motion is increased, however, it becomes increasingly difficult to obtain a uniform distribution of these larger size particles over the surface and ultimately to produce a coating having a uniform weight over the entire surface subjected to atomisation.

For different coating combinations it has been found that the particles in the coatings may vary from as small as 15 microns in diameter to as large as 350 microns in diameter and that most coatings comprise a mixture of particle sizes. When the particle sizes in the atomised coating material form particles in the coating within this range it is possible to regulate the temperatures of the substrate and the rate of relative motion between the source of the particles and the substrate being coated to obtain a uniform coating. It is even possible to prepare coatings useful for certain purposes when some of the particles in the coating exceed the size of 350 microns and range as high as about 500 microns in diameter, but such coatings are usually less uniform and thus less desirable for most applications than the coatings including the above small range of particle sizes.

As a general guide to selecting the optimum operating conditions for the selected substrate and coating material it may be pointed out that for a given size of particle atomised toward the surface at a fixed rate, the resulting coating tends to increase in weight as the temperature is increased. At a given temperature and a fixed size of particle emanating from the atomising nozzle, an increase in the rate of relative motion between the atomising nozzle and the surface to be coated results in a lower coating weight and ultimately will produce non-uniformity in the coating. Under fixed conditions of temperature and relative motion between the atomising nozzle and the surface to be coated, increasing the particle size tends to increase the coating formed and ultimately results in coalescence or piling up of the particles or running of the applied coating or both. As a lower limit, the weight of coatings whose purpose is to improve corrosion resistance or enhance paint receptivity should be at least 7 to 10 mg./sq. ft. With chromic acid and chromate-containing solutions an improved result is obtained with coating weights lower than 7 mg./sq. ft. and even as low as 2 to 5 mg./sq. ft. particularly where the chromate-containing solution is applied as a rinse over integral chemical coatings. For the majority of the solutions of this invention such as the phosphates, oxalates, oxides, etc., it is preferred to form a coating weighing at least 20 to 50 mg./sq. ft. With these guides in mind it is relatively easy to arrive at the optimum conditions by a few simple tests under operating conditions.

In applying the coating composition care should be taken not to direct the particles at the surface at too high a velocity or at too acute an angle, as this may cause an appreciable proportion of them to bounce off the surface. It is also important that the surface should be substantially free of water at the moment of impact of the atomised particles of the coating composition. In the presence of a continuous film of water on the surface the discrete particles tend to slide or migrate on the surface rather than remain stationary in the position of impact, and this results in a non-uniform coating.

The coating compositions may be atomised by means of any conventional spray guns or nozzles that are capable of forming small enough particles. Both internal and external mixing types of spray guns may be used, with either suction or pressure feed of the composition into the propellent chamber. Relatively dilute solutions can satisfactorily be applied using suction feed spray guns, but somewhat better results are obtained from the use of pressure on the coating-forming solution as

well as on the propellent. Installations for coating large areas of continuously moving surface may include multiple jets arranged on suitably spaced headers.

Any readily compressible gas which does not liquefy or solidify at low pressures and does not produce undesirable side effects is satisfactory as a propellent. However, air and steam are preferred, because they are inexpensive, readily available and perform well. Superheated steam has been found to be an especially good propellent. It atomises well and because of its condensation on contact with cooler air it decreases the volume of the spray and thus prevents any toxic elements which might be present in the spray from drifting off into the surrounding air. It is therefore the preferred propellent when ventilation is a problem. Low quality steam should not be used, since the water content causes the condensation of its moisture on the metal surface during the spraying process.

As mentioned above, the coating may be built up to any desired thickness by repeated applications of the aqueous coating composition in the same way as has already been described, the metal being reheated if necessary between applications. The weight of the coating applied in any particular case will depend on the intended use. For example, a coating applied to impart corrosion resistance preferably has a weight in the range 150 to 450 mg./sq. ft. whereas a coating applied for wear resistance or lubricating purposes preferably has a weight in the range 750 to 2000 mg./sq. ft. Paint base coatings are generally lighter, for example 50 to 200 mg./sq. ft.

Since in working according to this invention a coating solution is used once only it is not necessary to provide a second replenishment solution of different composition.

The following Examples, which in no way limit the scope of the invention, illustrate the formation of various different types of coating according to the invention and the properties of the coatings obtained.

### Example I

A number of 4" × 6" panels of an aluminium alloy containing 1—2% magnesium were cleaned by immersion in a 3 oz./gallon aqueous solution of sodium pyrophosphate for five minutes, removed, rinsed and thereafter heated in air to a temperature of about 200°F.

An aqueous solution was prepared to contain:

| | Grams |
|---|---|
| $H_3PO_4$ (75%) | 259 |
| $HNO_3$ (42° Baumé) | 290 |
| ZnO | 162 |
| $ZnSiF_6.6H_2O$ | 50 |
| Water to make 2000 ml. | |

This liquid was placed in a suction feed type MBCL " DeVilbiss " atomizing gun (DeVilbiss catalogue I-2801) provided with a No. 32 LE nozzle and a 1115 ES liquid feed nozzle 0.070 inches in size, and atomised using a line pressure of 70 p.s.i.g. with the liquid nozzle opened one-fourth of a turn from its closed position. (" DeVilbiss " is a Registered Trade Mark). Several of the cleaned and heated aluminium panels were coated with the coating solution by holding the gun about 8 inches from the panel surface and moving the nozzle across the panel surface at a speed of about 50 feet/minute, after which the panel was reheated with infra-red lamps to about 200°F. and coated with an additional similar pass. The panels were then cured for 3 minutes by heating in an air atmosphere furnace at 450°F. The complete coating weighed about 600 mg./sq. ft. Upon inspection the coatings were found to be uniformly distributed, hard, and light grey in colour. The coatings were insoluble in boiling hot water.

Three additional solutions were then prepared by modifying the above composition to contain 100, 150 and 300 grams of $ZnSiF_6.6H_2O$ respectively.

Further similar aluminium panels were coated with these solutions, using identical conditions to those described above. Upon inspection after curing all were found to have on their surfaces adherent coatings. As the quantity of $ZnSiF_6.6H_2O$ increased, the dullness of the light grey coating became more and more pronounced. The panels treated with the solution containing 150 grams $ZnSiF_6.6H_2$ had the most uniform coatings. In all other respects the panels were comparable.

### Example II

A solution of the following composition was prepared:

| | Grams |
|---|---|
| $H_3PO_4$ (75%) | 259 |
| $HNO_3$ (42° Baumé) | 290 |
| ZnO | 162 |
| $ZnSiF_6.6H_2O$ | 200 |
| $ZnF_2$ | 100 |
| Water to make 2000 ml. | |

Aluminium panels were prepared and coated with this solution as described in Example I. The coatings produced were similar in dullness to those resulting from the coating solution containing 300 grams $ZnSiF_6.6H_2O$ and slightly smoother but in other respects substantially the same.

### Example III

An aqueous solution was prepared to contain:

| | Grams |
|---|---|
| Zinc dihydrogen phosphate | 200 |
| $HNO_3$ (42° Baumé) | 140 |
| Ammonium silicofluoride $(NH_4)_2SiF_6$ | 75 |
| Water to make 2000 ml. | |

This solution was applied to the surface of aluminium panels similarly prepared and under identical conditions to those set forth above in Example I except the final coating weight was approximately 300 mg./sq. ft. Upon inspection, the panels were found to have on their surfaces an adherent, hard, light grey coating with a dullness comparable to that obtained in Example I from solutions containing 150 grams $ZnSiF_6.6H_2O$.

### Example IV

A solution was prepared to contain:

| | Grams |
|---|---|
| Ferric Nitrate | 100 |
| $H_3PO_4$ (75%) | 185 |
| Ammonium silicofluoride $(NH_4)_2SiF_6$ | 725 |
| Water to make 1000 ml. | |

This solution was applied to aluminium panels under the exact conditions set forth above in Example I. The resulting panels had a coating weight of about 150 mg./sq. ft. Upon inspection the panels were found to be coated with a uniform, hard, light metallic grey, slightly transparent coating on their surface which was insoluble in boiling hot water.

### Example V

The solution of Example IV was applied to 24 gauge mild steel panels 4″ × 6″ in size which had been cleaned by wiping with solvent followed by vapour degreasing. The panels were preheated to approximately 200°F. with infra-red lamps and coated using the conditions set forth above in Example I except the panels were not reheated between passes. The average coating weight was about 150 mg./sq. ft. These panels were uniformly coated with a dark grey coating having a slight yellow over-tone and the coating was insoluble in boiling hot water.

### Example VI

18/8 Austenitic stainless steel in the form of strips 4″ × 36″ × 0.14″ was coated with the following solutions:

*Solution A*

| | Grams |
|---|---|
| Ferrous oxalate | 46 |
| Oxalic Acid | 95 |
| $HNO_3$ | 300 |
| $HClO_3$ | 2C |
| Water to make 1000 ml. | |

*Solution B*

| | Grams |
|---|---|
| $Zn_3(PO_4)_2$ | 200 |
| $HNO_3$ (42° Baumé) | 260 |
| Water to make 1000 ml. | |

*Solution C*

| | Grams |
|---|---|
| $CaHPO_4.2H_2O$ | 200 |
| $HNO_3$ (42° Baumé) | 240 |
| Water to make 1000 ml. | |

*Solution D*

| | Grams |
|---|---|
| $MnHPO_4.3H_2O$ | 200 |
| $HNO_3$ (42° Baumé) | 320 |
| Water to make 1000 ml. | |

The stainless steel strips were first degreased and then heated in a furnace at 450°F. for about 3 minutes to thus raise their temperature to about 250°F. The heated strips were then coated with solutions A, B, C and D, using the equipment and spraying conditions set forth in Example I except that the panels were not heated between passes. The coatings were cured by positioning the strips in the furnace at a temperature of 450°F. and leaving them therein for about 3 minutes. Upon withdrawal the coatings were carefully inspected and all found to have an approximate coating weight of about 200 mg./sq. ft. The strips to which solution A was applied had a slight yellow, hard, uniformly distributed, extremely adherent coating which was insoluble in hot water. The strips coated with solution B were covered with a uniform, hard, slightly off-white powdery coating which was insoluble in hot water. The strips coated with solution C were similar in appearance to those coated with solution B except that the coatings were slightly more adherent. The strips coated with solution D had a light pink, uniformly distributed, hard, adherent, water-insoluble coating.

A number of 4″ × 12″ mild steel, copper and hard rolled magnesium panels were also sprayed with solutions A, B, C, and D using the same procedure. The coating formed on each weighed about 400 mg./sq. ft. The coatings resulting from the application of solution A were similar in appearance to those formed on stainless steel except that those on the copper panels were yellowish bronze in colour. The mild steel panels coated with solution D were purple in colour instead of pink. In all other respects no difference could be detected between the coatings on mild steel, copper and magnesium and those obtained on stainless steel from similar solutions.

### Example VII

This example illustrates the variations in

particle size and coating weight which result from alterations in the atomizing conditions of application. Several 4′ × 6′ panels of low carbon steel were cleaned by conventional methods and then preheated to a temperature in the range of about 350°F. to about 400°F. An aqueous admixture was prepared containing 2% $CrO_3$ and 1% polyacrylic acid. This aqueous admixture was placed in a "DeVilbiss"-type AGA spray gun using nozzle G and a 763 air cap, the liquid aperture in the nozzle being 0.026″ diameter. This equipment is described in detail in DeVilbiss catalogue IE—E, and is a spray gun using pressure on the aqueous admixture in the tank and a separate source of gaseous propellent. The pressure employed on the propellent, air, was 60 psig., and the pressure in the tank was 20 psig. With the rate of relative motion between the spray gun and the panels of approximately 60 feet/minute a single pass over the surface produced on the panels a coating weight in the range of 2 to 5 mg./sq. ft. The coatings were cured by heating the panels in an oven at a temperature of 375°F. for about 3 minutes and then withdrawing them. An inspection of the coated surface showed irregular coated areas separated by uncoated areas.

Another set of similarly cleaned panels were atomization coated in the some way with the same solution, the pressure on the chromic acid-polyacrylic acid admixture being increased to 25 psig. The cured coatings which resulted from a single pass of the atomizing gun over the surface at the same speed weighed between 5 and 10 mg./sq. ft.

Another set of similar panels was atomization coated in the same way with the same admixture, the pressure on the admixture being increased to 40 psig. After one pass over the surface at the same relative speed, and curing, an inspection of the surface showed a coating having a weight in the range 10 to 15 mg./sq. ft., but in this case the coating was interspersed with globules of coating, some of which were as large as about 1 mm, in diameter.

All three sets of coated panels were painted with a white primer coat and a white enamel finish coat and were tested for corrosion resistance by spraying with a 20% sodium chloride solution. After 312 hours in the salt spray chamber the panels resulting from the use of 20 psig. pressure on the coating admixture were found to be only about one-half as resistant to corrosion as those panels resulting from the use of 25 and 40 psig. pressure on the coating admixture.

The particle size of the particles resulting from use of the 20 and 25 psig. pressures on the liquid admixture was approximately the same but with the lower pressure the rate of flow of the coating admixture relative to the rate of traverse of the surface was insufficient to produce a quantity of coating to provide the desired surface protection. By increasing the pressure on the coating material to 25 psig. and maintaining the air propellent pressure of 60 psig. the coating weight was increased ro 5—10 mg./sq. ft., which was a sufficient quantity of material to provide the desired surface protection. When the pressure on the chromic acid-polyacrylic acid admixture was increased to 40 psig. however, the particles which resulted were irregular in size and much larger and the resulting coating included the non-uniformity spaced globular particles.

On increasing the pressure on the air propellent to 80 psig. while maintaining the pressure on the chromic acid-polyacrylic acid admixture at 40 psig uniformly sized particles were again produced which, upon spraying similar panels under similar conditions gave a uniform coating having a weight of about 20 mg./sq. ft. When these panels were painted in a comparable fashion and tested for corrosion resistance they were found to be even better in corrosion resistance than the panels containing 5—10 mg./sq. ft.

### Example VIII

A group of zinc coated steel panels 4″ × 6″ × 1/16″ was heated to 160°F, and another group of comparable panels was heated to 450°F. Two aqueous compositions were prepared, one of which contained 2% chromic acid and 2% polyacrylic acid weight/volume, and the other of which contained 2% polyacrylic acid and 4% chromic acid, weight/volume. Each of these aqueous admixtures was placed in an MBCL spray gun having a 32 LE nozzle, 0.070″ liquid feed nozzle diameter, (DeVilbiss catalogue I—2801) and the panels were coated by employing an air propellent pressure of 60 psig. and a rate of flow of the admixture of about 1 quart/hour. Under these conditions the spray particles had a size in the range 3 to 25 microns and after curing the coatings by positioning the panels for about 3 minutes in an oven at 375°F., the coatings were found to have a typical metallic appearance, slightly glossy and to be uniformly distributed over the surface. The coatings were hard, had a weight in the range 18 to 36 mg./sq. ft. and were insoluble in boiling hot water. These panels were tested for humidity resistance by subjecting them to a humid atmosphere for one week, and upon inspection they were all found to be substantially free from white corrosion products.

### Example IX

Another set of 4″ × 6″ aluminium panels were prepared for coating as set forth in Example I. The following aqueous solutions were compounded:

*Solution A*

| | Grams |
|---|---|
| $H_3PO_4$ (75%) | 259 |
| $HNO_3$ (42° Baumé) | 140 |
| ZnO | 162 |
| $H_3BO_3$ | 146 |
| HF (60%) | 202 |
| $ZnSiF_6.6H_2O$ | 315 |
| Water to make 2000 ml. | |

*Solution B*

| | Grams |
|---|---|
| $H_3PO_4$ (75%) | 259 |
| $HNO_3$ (42° Baumé) | 140 |
| ZnO | 162 |
| $H_3BO_3$ | 219 |
| HF (60%) | 202 |
| Water to make 2000 ml. | |

The panels were atomization coated with each of these solutions in an identical manner to that set forth in Example I, cured similarly, and upon inspection were found to be coated with a uniform light grey coating which was hard and adherent. These coatings, when subjected to boiling hot water, were found to be partially if not completely soluble therein.

EXAMPLE X

Alkaline chromate aqueous solutions were compounded to contain the following:

*Solution A*

| | Grams |
|---|---|
| $(NH_4)_2SO_4$ | 30 |
| $(NH_4)_2CR_2O_7$ | 30 |
| $NH_4OH$ | 2.5 |
| Water to make 2000 ml. | |

*Solution B*

| | Grams |
|---|---|
| $(NH_4)_2SO_4$ | 15 |
| $Cr_2(SO_4)_3$ | 15 |
| $(NH_4)_2Cr_2O_7$ | 100 |
| Water to make 2000 ml. | |

Solutions A and B were applied to panels prepared in accordance with Example I under the exact conditions there stated, and after curing the panels were found to have on their surfaces slightly non-uniform dark yellow coatings when the coating weight was about 150 mg./sq. ft. Other panels were coated with the same solutions to form coating weights in the range of 400—6000 mg./sq. ft., and these panels were coated with a granular coating which became blacker as the coating weight increased toward 600 mg./sq. ft. The yellowish coatings were partially soluble in boiling water and as the coating became darker in appearance the solubility in water decreased.

EXAMPLE XI

4″ × 6″ aluminium panels cleaned in accordance with the procedure of Example I were atomization coated with the following solution:

| | Grams |
|---|---|
| $H_3PO_4$ (75%) | 250 |
| $HNO_3$ (42°Bé) | 290 |
| ZnO | 162 |
| $ZnSiF_6.6H_2O$ | 300 |
| Chromic or molybdic acid | 0.5—1.5 |
| Water to make 2000 ml. | |

This solution was applied in accordance with the procedure of Example I and the coatings, upon inspection, were similar in appearance to those obtained in Example I.

A number of mild steel panels, at a temperature of about 250°F., were coated with this solution in accordance with the procedure of Example I except the panels were not reheated between passes. Another set of mild steel panels was coated, under identical conditions, with a solution similar to the above except that it contained no chromic or molybdic acid. In both cases uniform coatings were produced but somewhat better humidity resistance was found to be characteristic of the panels resulting from the solution containing the chromic or molybdic acid inhibitor.

EXAMPLE XII

18—8 stainless steel panels were atomization coated with a solution containing 40 cc. of 36% HCl, 10 grams of sodium sulphite and water to make one gallon. Panels were heated to a temperature of about 200°F. and coated with a solution in accordance with the procedure of Example VI. The resulting panels were uniformly coated with an adherent sulphide coating, a part of which was soluble in water.

The same solution was used to atomization coat mild steel panels preliminarily heated to about 250°F. The coatings obtained were uniformly distributed adherent dark sulphide coatings.

EXAMPLE XIII

Mild steel panels preheated to about 250°F. and atomization coated with an aqueous solution containing sodium dihydrogen phosphate which upon analysis was found to contain in percent weight/volume:

| | Percent |
|---|---|
| $PO_4$ | 1.0 |
| $ClO_3$ | 0.6 |

This solution was found to have a total acid of 10.3. A number of these panels were coated under the conditions specified in Example VI, and on inspection were found to be coated with a grey adherent phosphate coating of typical appearance.

### EXAMPLE XIV

4" x 6" cold rolled steel panels were solvent cleaned and coated by conventional spray application of an aqueous solution containing zinc 0.14%, $PO_4$ 0.75%, nitrate ($NO_3$) 1.8%, all percentages being weight per volume. The solution had a free acid of 0.7 and a total acid of 10.1. With the solution at a temperature of 135°F. the panels were spray flooded with the solution for a one minute period of contact to produce coatings having an average weight of about 265 mg./sq. ft. These panels were preheated to a temperature in the range 175—200°F. in an air atmosphere furnace maintained at a temperature of about 300°F. Groups of these heated phosphate coated panels were then atomization coated with various hexavalent chromium-containing rinse solutions by employing the atomization equipment identified in Example I. After application of the rinse solutions certain of the panels were cured by positioning them in a furnace at 300°F. for 30 seconds and withdrawing while others of the panels were positioned for 3 minutes in the same furnace prior to withdrawal. The thus coated panels were tested for salt spray resistance in comparison with panels of the same steel which were uncoated and which were similarly phosphate coated and rinsed in a conventional chromic acid liquid solution in the current commercial manner. Other panels were painted with a primer and a finish white enamel and these panels were scratched diagonally from corner to corner to form an X on the painted surface and tested for salt spray resistance as well as humidity. The relative results of these tests are summarized in Table I.

TABLE I

| Test No. | Atomization Rinse Percent by Wt. | Curing | Ctg. Wt. Mg/ft² | Hours in Salt Spray | | | | | | | | Hrs. in Humidity | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Bare Coating | | | | | Painted | | | Painted | | |
| | | | | 2 | 3 | 4 | 5 | 7 | 144 | 288 | 504 | 144 | 312 | 504 |
| 1 | $.1CrO_3$—$.1H_3PO_4$ | Air Dried | 16 | 3L | 4ML | 5ML | 5M | — | 0 | 0 | 0 | 0 | $B_1$ | $B_1$ |
| 2 | $.05CrO_3$—$.05H_3PO_4$ | Air Dried | 8 | 5L | 5ML | 5ML | 5M | — | 0 | 0 | 0 | $B_1$ | $B_2$ | $B_2$ |
| 3 | $.1CrO_3$ | Air Dried | 5 | 5L | 5M | — | — | — | 0 | 0 | 0 | 0 | $B_1$ | $B_1$ |
| 4 | Sol. I—$.05CrO_3$ | 30 seconds at 300° F. | 5 | 5M | — | — | — | — | 0—1 | 0—1 | 1—3 | 0 | 0 | $B_1$ |
| 5 | Sol. I—$.5CrO_3$ | 30 seconds at 300° F. | 50 | 1L | 4L | 5ML | 5ML | 5M | 0 | 0 | 0 | $B_1$ | $B_1$ | $B_1$ |
| 6 | Sol. II—$.05CrO_3$ | 3 minutes at 300° F. | 4 | 5ML | 5ML | 5M | — | — | 1—1 | 2—3 | 3—7 | 0 | 0 | 0 |
| 7 | Sol. III—$.05CrO_3$ | 3 minutes at 300° F. | 4 | 5M | 5M | — | — | — | 0 | 0—1 | 0—1 | 0 | 0 | $B_1$ |
| 8 | Sol. I—$.5CrO_3$ | 3 minutes at 300° F. | 50 | 0 | 1.5L | 1.5L | 2L | 4L | 0 | 0 | 0 | $A_1$ | $A_1$ | $A_1$ |
| 9 | Bare Controls | — | — | 5M | — | — | — | — | 1—1 | 2—3 | 4—9 | 0 | 0 | $B_1$ |
| 10 | $.01CrO_3$—$.015H_3PO_4$ | 3 minutes at 300° F. | Control | 5M | — | — | — | — | 1—1 | 2—3 | 4—7 | $B_1$ | $B_1$ | $B_1$ |

I—3% $CrO_3$, 1.5% Polyacrylic acid (25%), 1.8% $PO_4$ as Zn $(H_2PO_4)_2.2H_2O$

II—4% $CrO_3$, 2% Polyacrylic acid (25%), 1% $PO_4$ as Zn $(H_2PO_4)_2.2H_2O$

III—3% $CrO_3$, 1.8% $PO_4$ as Zn $(H_2PO_4)_2.2H_2O$ (In each case, solutions I, II and III were diluted to produce the $CrO_3$ concentration shown)

In Tables I, II and III, the salt spray resistance, bare coating, is reported on the basis of the proportion of the surface coated with rust ranging between 1 and 5, 1 being a small portion of the surface and 5 being the total surface. L is light rust, VL is very light rust and M is medium rust so that, for example, 5 M means that the panel is entirely coated with medium rust. The salt spray resistance of the painted panels is reported on the basis of the number of sixteenths of an inch which rust had proceeded from the scratch marks diagonally across the panel. Zero means no rusting, 0—1 means rust has proceeded a maximum of one-sixteenth of an inch and a minimum of zero, whereas 4—9 means that the rust has migrated a maximum distance of nine-sixteenths of an inch and a minimum of four-sixteenths along the diagonals. Humidity is reported on the basis that A indicates bottom edge blistering and B indicates surface blistering while the subscripts vary between 1 and 5 and $B_5$ indicates severe blistering over the entire surface.

On this comparative basis it can be seen that tests 1, 2 and 3 all gave better bare coating resistance in salt spray than the controls. Excellent spray and humidity results were obtained, bare and painted, in tests 5 and 8 in which the coating weights are extremely heavy relative to coating weights obtainable with normally employed aqueous solution rinsing techniques. In each of these cases there was no rundown and no problem of chromic acid build-up at the draining edges of the panels as is characteristic of normally rinsed parts.

EXAMPLE XV

A large number of 4" x 6" cold rolled steel panels were solvent cleaned, degreased and rag wiped and then immersed in an aqueous solution containing 0.4% Zn, 1.6% $PO_4$, 1% $NO_3$, and 0.2% ferrous ion, the solution having a total acidity of 30.2 (total acidity of 10 ml sample titrated to phenolphthalein endpoint with N/10 sodium hydroxide). This solution was heated to 185°F. and the panels immersed therein for 30 minutes and withdrawn. This resulted in the formation of a zinc phosphate coating having an average weight of 1000 to 1500 mg./sq. ft. These coated panels were then heated in an air atmosphere furnace at 300°F. for approximately 20 seconds to raise their temperature to 175 to 200°F. The panels were then atomization coated using the apparatus of Example II and the general procedure there described, except that the rinse solutions were modified in composition and the thickness of the dried solutions varied as set forth below in Table II, which shows the comparative results of salt spray tests on the panels. Certain of the panels, after atomization coating but before subjected to salt spray testing, were oiled by dipping the coated panels in a commercial oiling composition comprising zinc stearate thinned with mineral spirits, removing them and allowing them to dry. Control tests for salt spray resistance were carried out on identical bare panels and on panels which received similar phosphate coating and typical commercial rinsing in an aqueous dilute hexavalent chromium rinse solution containing about 0.01% $CrO_3$ and 0.015% $H_3PO_4$.

TABLE II

| Test No. | Atomization Rinse Percent by Wt. | Curing | Ctg. Wt. Mg/ft² | Hours in Salt Spray | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Dry | | | | | | | Oiled | | | |
| | | | | 2 | 4 | 6 | 10 | 14 | 20 | 26 | 24 | 48 | 118 | 190 |
| 1 | $.5CrO_3$—$.5H_3PO_4$ | Air Dried | 75 | 0 | 0 | 3L | 5L | 5L | 2 | 4 | 0 | 0 | 2 | 3.5 |
| 2 | $1CrO_3$—$1.5H_3PO_4$ | Air Dried | 150 | 0 | 0 | 0 | 0 | 1 | 2 | 3 | 0 | 0 | 1 | 2 |
| 3 | 1% $CrO_3$ | Air Dried | 50 | 0 | 0 | 0 | 2L | 1 | 3 | 4 | 2 | 2 | 3 | 4 |
| 4 | Sol. I—$.5CrO_3$ | 30 seconds at 300° F. | 35 | 5VL | 5L | 5L | 5L | 5L | 2 | 3 | 1 | 1 | 1.5 | 5 |
| 5 | Sol II—$.5CrO_3$ | " | 35 | 4VL | 5L | 5L | 5L | 5L | 5ML | 5 | 1 | 1 | 1 | 3 |
| 6 | Sol. III—$.5CrO_3$ | " | 50 | 4VL | 5L | 5L | 5L | 5 | — | — | 0 | 1 | 1.5 | 3 |
| 7 | Sol. IV—$.5CrO_3$ | " | 35 | 2VL | 5VL | 4 | 5 | — | — | — | 2 | 2 | 3.5 | 5 |
| 8 | Sol. V—$.5CrO_3$ | " | 40 | 4VL | 5VL | 5VL | 5 | — | — | — | 0 | 0 | 2.5 | 5 |
| 9 | Sol. I—$.5CrO_3$ | 3 minutes at 300° F. | 35 | 0 | 0 | 0 | 0 | 1 | 2 | 3 | 0 | 0 | 5L | 5 |

TABLE II—*cont.*

| Test No. | Atomization Rinse Percent by Wt. | Curing | Ctg. Wt. Mg/ft² | Hours in Salt Spray | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Dry | | | | | | | Oiled | | | |
| | | | | 2 | 4 | 6 | 10 | 14 | 20 | 26 | 24 | 48 | 118 | 190 |
| 10 | Sol. II—.5$CrO_3$ | " | 35 | 5VL | 5L | 5L | 5L | 5L | 1 | 3 | 0 | 0 | 1 | 5 |
| 11 | Sol. III—.5$CrO_3$ | " | 50 | 1L | 1L | 1 | 2 | 3 | 5 | — | 1.5 | 1.5 | 2 | 5 |
| 12 | Sol. IV—.5$CrO_3$ | " | 35 | 1L | 5L | 4 | 5 | — | — | — | 0 | 0 | 3 | 5 |
| 13 | Sol. V—.5$CrO_3$ | " | 40 | 5VL | 5L | 5L | 5 | — | — | — | 0.5 | 1 | 1.5 | 5 |
| 14 | Bare Control | — | — | 5M | — | — | — | — | — | — | 0 | 0 | 3 | 5 |
| 15 | Phosphate Coated Rinsed 0.01$CrO_3$ .015 $H_3PO_4$ | Control | — | 5M | — | — | — | — | — | — | 0 | 0 | 5 | — |

I—4% $CrO_3$, 2% Polyacrylic acid (25%), 1% $PO_4$ as Zn $(H_2PO_4)_2.2H_2O$

II—3% $CrO_3$, 1.8% $PO_4$ as $Zn(H_2PO_4)_2.2H_2O$

III—3% $CrO_3$, 1.5% Polyacrylic acid (25%), 1.8% $PO_4$ as $Zn(H_2PO_4)_2.2H_2O$

IV—3% $CrO_3$, 1.5% Polyacrylic acid (25%), 1.8% $PO_4$ as $Zn_3(PO_4)_2$

V—3% $CrO_3$, .7% ZnO, 1.8% $PO_4$ as $H_3PO_4$ (85%)

By inspecting Table II it may be seen that the air dried rinses of tests 1, 2 and 3 showed considerable improvement in salt spray resistance relative to the controls and test 2 is outstanding in corrosion resistance, the $CrO_3$ coating being 150 mg./sq. ft. Tests 4 to 13 showed that all of the samples were substantially better than the controls, in both dry and oiled form where 30 seconds and 3 minutes were used for curing the coating.

EXAMPLE XVI

A large number of 4" × " cold rolled steel panels were solvent cleaned, degreased and rag wiped and then immersed in an aqueous solution containing 3.75% $PO_4$, 0.04% Ni, 0.56% Mn, 0.2% $NO_3$ and 1.8% $Fe^{++}$ and having a free acid of 2.0 and a total acid of 12.0 (2 ml sample titrated to phenolphthalein endpoint with N/10 sodium hydroxide). The cleaned panels were immersed in the solution at 200°F., allowed to remain therein for 15 minutes and withdrawn, after which they were found to be coated with an average coating weight between about 900 and 1200 mg./sq. ft. All of the panels were atomization coated with various hexavalent chromium-containing solutions. Certain of the panels were oiled and all were tested for resistance to corrosion in a 20% sodium chloride salt spray for various times, relative to both bare controls and phosphate coated controls conventionally rinsed in a solution containing .01% $CrO_3$ and .015% $H_3PO_4$. The results of these tests are summarized in Table III.

TABLE III

| Test No. | Atomization Rinse Percent by Wt. | Curing | Ctg. Wt. Mg./ft$^2$ | Hours in Salt Spray | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Dry | | | | | | | Oiled | | | |
| | | | | 2 | 4 | 6 | 10 | 14 | 20 | 26 | 24 | 48 | 118 | 190 |
| 1 | $.05CrO_3$—$.05H_3PO_4$ | Air Dried | 8 | 0 | 2L | 3L | 4 | 5 | — | — | 0 | 0 | 1 | 5 |
| 2 | $0.1CrO_3$—$.11H_3PO_4$ | " | 16 | 0 | 0 | 0 | 2L | 2 | 3 | 5 | 0 | 0 | 1 | 5 |
| 3 | $0.5CrO_3$—$0.55H_3PO_4$ | " | 75 | 0 | 0 | 3L | 4 | 5 | — | — | 0 | 0 | 2 | 5 |
| 4 | $CaCr_2O_7$(pH About 4) —$1Cr_2O_3$ | " | 100 | 0 | 0 | 1L | 3L | 5 | — | — | 0 | 1L | 5 | — |
| 5 | Sol. II—$.5CrO_3$ | 30 seconds at 300° F. | 35 | 4L | 5 | — | — | — | — | — | 0 | 0 | 5 | — |
| 6 | Sol. III—$0.5CrO_3$ | " | 50 | 0 | 0 | 0 | 2L | 5 | — | — | 0 | 0 | 5 | — |
| 7 | Sol. V—$0.5CrO_3$ | " | 40 | 0 | 1L | 3L | 5L | 5 | — | — | 0 | 0 | 3 | 5 |
| 8 | Sol. II—$.5CrO_3$ | 3 minutes at 300° F. | 35 | 0 | 0 | 0 | 2L | 2 | 3 | 5 | 0 | 0 | 3 | 5 |
| 9 | Sol. III—$.5CrO_3$ | " | 50 | 0 | 1L | 2L | 5L | 5 | — | — | 0 | 0 | 1 | 5 |
| 10 | Sol. V—$.5CrO_3$ | " | 40 | 0 | 0 | 1 | 5L | 5 | — | — | 0 | 0 | 0 | 5 |
| 11 | Bare Controls | — | — | 5L | 5 | — | — | — | — | — | 0 | 0 | 5 | — |
| 12 | Phosphate coated immersion rinsed $0.01CrO_3$—$.01H_3PO_4$ | Control | — | 5L | 5 | — | — | — | — | — | 0 | 0 | 5 | — |

II—3% $CrO_3$, 1.8% $PO_4$ as $Zn(H_2PO_4)_2.2H_2O$

III—3% $CrO_3$, 1.5% Polyacrylic acid (25%), 1.8% $PO_4$ as $Zn(H_2PO_4)_2.2H_2O$

V—3% $CrO_3$, .7% $ZnO$, 1.8% $PO_4$ as $H_3PO_4$ (85%)

An inspection of this Table shows substantial improvement in salt spray resistance both dry and oiled for light and heavy weight coatings relative to the controls.

EXAMPLE XVII

Lubricating and corrosion-resistant coatings were formed by atomization spraying on mild steel panels having a temperature of about 250°F. one of the following dispersions: monolauryl phosphate—160 grams; morpholine—32 grams; zinc acetate—25 grams; sodium chlorate—35 grams; 0.4% sodium meta-nitro benzene sulphonate; each mixed with distilled water to make 2 gallons. The equipment and the basic procedure described in Example 1 were used. The coatings formed were uniformly distributed and crushed to an unctuous film upon the application of pressure.

WHAT WE CLAIM IS:—

1. A process for forming a protective coating on a metallic surface by treatment with an aqueous coating composition which interacts with the surface or with an integral coating thereon which comprises preheating the surface and applying the coating composition in the form of finely divided particles, the temperature of the surface and the size and quantity of the particles being so correlated that the particles dry substantially in the position where they first strike the surface.

2. A process according to claim 1 in which the temperature of the surface is maintained at at least 135°F during the application of the coating composition.

3. A process according to claim 1 or claim 2 in which the surface is preheated to a temperature of 175—800°F before the application of the coating composition.

4. A process according to any of claims 1 to 3 in which the temperature of the surface is such that when the particles strike the surface the interaction between the coating composition and the surface and the drying of the particles are substantially instantaneous.

5. A process according to any of claims 1 to 3 in which further heat is supplied to the surface during the application of the coating.

6. A process according to any of claims 1 to 5 in which the coated surface is further heated after the coating has been applied in order to cure the coating.

7. A process according to any of claims 1 to 6 in which the thickness of the coating is increased by further applications of the coating composition in the same manner.

8. A process according to any of the preceding claims in which the aqueous coating composition is applied in the form of particles having a size in the range 15—350 microns.

9. A process according to any of the preceding claims in which the finely divided particles are formed and applied to the surface by atomising the aqueous coating composition with a gaseous propellent.

10. A process according to claim 9 in which the surface is progressively coated by moving it relative to the source of atomised particles.

11. A process according to any of the preceding claims in which volatile material is continuously removed from the neighbourhood of the surface being coated.

12. A process according to any of the preceding claims in which the aqueous coating composition is an aqueous acidic phosphate solution.

13. A process according to any of claims 1 to 11 in which the aqueous coating composition is an aqueous acidic solution containing hexavalent chromium.

14. A process according to claim 13 in which the aqueous coating composition also contains an organic polymeric or resinous film-forming ingredient.

15. A process according to claim 14 in which the film-forming ingredient is polyvinyl alcohol or polyacrylic acid.

16. A process for improving the corrosion resistance of a metallic surface which comprises forming a phosphate coating on it and subsequently coating it in accordance with any of claims 13 to 15.

17. A process according to claim 1 substantially as described in any of Examples I to XVII.

18. A metallic article having on its surface an adherent integral coating produced by the process of any of claims 1 to 15.

19. A metallic article having on its surface a phosphate coating and an overlayer of a material containing hexavalent chromium produced by the process of claim 16.

For the Applicants:—
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51—52, Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

02 - B - 190 - A WO

(51) Int. Cl. 2: **C 23 F 7/08**

(19) BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENTAMT

DE 29 09 698 A 1

# (11) Offenlegungsschrift 29 09 698

| | | |
|---|---|---|
| (21) | Aktenzeichen: | P 29 09 698.8 |
| (22) | Anmeldetag: | 12. 3. 79 |
| (43) | Offenlegungstag: | 27. 9. 79 |

(30) Unionspriorität:

(32) (33) (31) 14. 3. 78 Belgien 6-46388

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(54) Bezeichnung: Verfahren zur Oberflächenbehandlung von Metallband


(71) Anmelder: Centre de Recherches Metallurgiques - Centrum voor Research in de Metallurgie - Association sans but lucratif - Vereniging zonder winstoogmerk, Brüssel

(74) Vertreter: Plöger, U., Dipl.-Ing., Pat.-Anw., 4000 Düsseldorf

(72) Erfinder: Hancart, Jules, Jupille; Paulus, Philippe, Lüttich (Belgien)


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DE 29 09 698 A 1


9. 79 909 839/788 8/80

PATENTANWALT
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TELEFON 71 32 34 und 71 89 97
TELEX 8 587 941

10.3.1979
Pl/R

REG. NR. 3399

2909698

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CENTRUM VOOR RESEARCH IN DE METALLURGIE
Association sans but lucratif
Vereniging zonder winstoogmerk
47, rue Montoyer Brüssel / BELGIEN

# Verfahren zur Oberflächenbehandlung von Metallband

## PATENTANSPRÜCHE:

1. Verfahren zur Oberflächenbehandlung von Metallband und Aufbringen eines Phosphatbelages auf dasselbe, dadurch gekennzeichnet, daß es die nachstehenden Verfahrensschritte aufweist:

   a) Erhitzen des Bandes auf eine oberhalb 250°C und insbesondere oberhalb 300°C liegende Temperatur, vorzugsweise unter Schutzgas, wenn die Temperatur der Beheizung über 500°C beträgt, und

   b) Abschrecken des Bandes in einem Bad mit einer Temperatur von 80°C oder darüber, vorzugsweise von 90°C oder darüber, welches Bad ein oder mehrere Phosphate des Types $M_e\ (H_2PO_4)_n$ enthält, wobei $M_n$ Zn, Ni, Mn

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oder ein Alkalimetall sein kann, und wobei die Konzentration zwischen 1 und 20 g/l, vorzugsweise zwischen 5 und 15 g/l beträgt, und wobei das Bad wahlweise noch eine anorganische Säure, vorzugsweise Phosphorsäure, sowie einen Reaktionsbeschleuniger des Types Molybdat und ein nicht schäumendes Detergenz enthalten kann.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das pH der Lösung zwischen 3 und 6 liegt.

3. Verfahren nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß phosphatierende Salze zugefügt werden.

4. Verfahren nach den Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß das mit dem Überzug zu versehene Band ein Stahlband ist.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß das Beschichten des Bandes im Verlaufe einer Wärmebehandlung erfolgt, bei welcher das Band zur schnellen Abkühlung nach der Rekristallisation in eine heisse wässerige Lösung eingebracht wird und wahlweise noch in eine weitere heisse wässerige Lösung zwecks abschliessender Kühlung nach der Überalterungs-Wärmebehandlung eingeführt wird, wobei die eine bzw. die andere dieser Lösungen als ein Phosphatierungsbad Anwendung finden.

6. Verfahren nach den Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß ein einziges Eintauchen während einer Dauer zwischen 0,5 und 40 Sekunden durchgeführt wird.

7. Verfahren nach den Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß die Phosphatierungsbehandlung kombiniert mit der Wärmebehandlung mit Abschreckung im Anschluss an das Rekristallisationsglühen, jedoch ohne Vergütung (bei zum Beispiel hochfestem Stahl) derart ausgeführt wird, daß die Phosphatierung im Verlauf der Abschreckung durchgeführt wird.

8. Verfahren nach den Ansprüchen 4 bis 6, dadurch gekennzeichnet, daß die nachstehenden Arbeitsgänge durchgeführt werden:

   a) Erhitzen auf eine Temperatur oberhalb der Rekristallisationstemperatur des Bleches und Einhalten dieser Temperatur für eine ausreichende Zeitdauer, wobei diese Erhitzung und Vorwärmung unter Schutzgasatmsophäre durchgeführt werden;

   b) Abschrecken in einem Phosphatierungsbad der vorbeschriebenen Art und mit einer Temperatur von 80°C oder höher, wobei die Badverweilzeit zwischen 0,5 und 40 Sekunden bei einer unter 150°C liegenden Temperatur beträgt;

   c) sehr gründliches Spülen des Bleches am Badausgang;

   d) Vergüten oder Überalterungsbehandlung durch Erhitzen des Bleches auf eine Temperatur zwischen 300°C und 500°C.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß die abschliessende Kühlung in an sich bekannter Weise und vor allem unter der Einwirkung von Strahlen der Umgebungsluft durchgeführt wird.

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10. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Band nach der Überalterungsbehandlung erneut in einer Passivierungslösung abgeschreckt wird, welche insbesondere eine Mischung von $Cr^{3+}$-$Cr^{6+}$ aufweist.

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BESCHREIBUNG:

Die Erfindung bezieht sich auf ein Verfahren zur Beschichtung eines Metallbandes, und zwar insbesondere eines für das Tiefziehen vorgesehenen Metallbandes, mit einem Phosphatbelag, wobei diese Behandlung im Verlaufe einer Wärmebehandlung durchgeführt wird.

Der Anwendungsumfang des Verfahrens sieht eine Beschichtung des Metallbandes, und zwar insbesondere eines Stahlbandes, mit einem Schutzbelag, wie einer Phosphatschicht, vor und ist sehr beträchtlich; den genannten Schutzfilm kann man beispielsweise in den nachstehenden Fällen mit Vorteil anwenden:

- zur Ausbildung eines vorübergehenden Oberflächenschutzes zwischen Herstellung und Verwendung;
- zur Herstellung einer Unterschicht, welche das Haften eines späteren Schutzbelages begünstigt;
- zur Ausbildung einer Unterlage als Vorbereitung für einen Anstrich und
- zur Ausbildung eines Belages, der das Haften eines Schmiermittels vor einer spanlosen Formgebung begünstigt.

Diese unterschiedlichen Anwendungsformen unterscheiden sich nur durch die Dicke und durch die Art des aufzubringenden Schutzfilms, insbesondere bei einem Phosphatbelag.

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So wurde von der Anmelderin schon ein Verfahren zur kontinuierlichen Wärmebehandlung von Stahlband vorgeschlagen. Dieses Verfahren besteht im wesentlichen darin, daß das Blech auf eine Tmperatur oberhalb seiner Rekristallisationstemperatur aufgeheizt wird und anschliessend eine schnelle Abkühlung durch Eintauchen in ein Wasserbad erfährt, dessen Temperatur über 75°C und vorzugsweise merklich über seiner Siedetemperatur gehalten wird.

Auch hat die Anmelderin bereits den gleichzeitigen Vorschlag der Verbindung der Wärmebehandlung mit einer Oberflächenbehandlung gemacht, um das Band mit einem metallischen Schutzbelag oder einem Phosphatbelag zu versehen.

Der vorliegenden Erfindung liegt die Aufgabe zugrunde, die Vorteile beider Behandlungen bei einer Phosphatierungsbeschichtung miteinander zu verbinden.

Dieses Verfahren basiert auf der Tatsache, daß im Zuge von seitens der Anmelderin durchgeführten Versuchen festgestellt werden konnte, daß sich die Auftragsgeschwindigkeit eines Phosphatbelages merklich erhöht, wenn das Blech nicht im kalten Zustand in das Bad eingetaucht wird, sondern vorher auf eine Temperatur über 250°C erhitzt wird. Auf Grund dieser überraschenden Tatsache kann das Metallband in sehr kurzer Zeit mit einem dicht anliegenden und verhältnismäßig dicken Film versehen werden.

Figur 1 zeigt den Verlauf der Auftragsgeschwindigkeit in Abhängigkeit von der Temperatur des Bleches bei seinem Eintritt in ein bekanntes Bad zur Phosphatierung, welches 8 g/l $NaH_2PO_4$ und Phosphorsäure ($H_3PO_4$) mit einem pH in der Grössenordnung von 4,7 und einer Temperatur von 97°C aufweist.

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Es konnte beobachtet werden, daß die nach den nachstehend beschriebenen Verfahren realisierbare Auftragsgeschwindigkeit noch stark erhöht werden kann, wenn das Blech vor dem Einleiten in das Bad einer Vorwärmbehandlung unterzogen wird. Andererseits läßt sich durch Einsatz einer Lösung der vorbeschriebenen Art die Oxydation des Bleches, die sich normalerweise beim Abschrecken von einer Temperatur über 500°C in beispielsweise destilliertem Wasser einstellt, vollständig vermeiden.

Auf der Grundlage dieser Betrachtungen ist das erfindungsgemäße Verfahren im wesentlichen durch die nachstehenden Verfahrensschritte gekennzeichnet:

a) Erhitzen des Bandes auf eine oberhalb 250°C und insbesondere oberhalb 300°C liegende Temperatur, vorzugsweise unter Schutzgas, wenn die Temperatur der Beheizung über 500°C beträgt, und

b) Abschrecken des Bandes in einem Bad mit einer Tmperatur von 80°C oder darüber, vorzugsweise von 90°C oder darüber, welches Bad ein oder mehrere Phosphate des Types $M_e (H_2PO_4)_n$ enthält, wobei $M_n$ Zn, Ni, Mn oder ein Alkalimetall sein kann, und wobei die Konzentration zwischen 1 und 20 g/l, vorzugsweise zwischen 5 und 15 g/l beträgt, und wobei das Bad wahlweise noch eine anorganische Säure, vorzugsweise Phosphorsäure, sowie einen Reaktionsbeschleuniger des Types Molybdat und ein nicht schäumendes Detergenz enthalten kann.

Erfindungsgemäß beträgt das pH der Lösung vorteilhaft 3 bis 6.

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Erfindungsgemäß ist es erforderlich, die notwendigen Mengen an phosphatierenden Salzen zuzusetzen, um den Konzentrationsrückgang des Bades zu vermeiden.

Das zur Anwendung gelangende Metallbad ist besonders vorteilhaft ein Stahlband.

Nach einer abgewandelten Ausführungsform des erfindungsgemäßen Verfahrens erfolgt die Beschichtung des Bandes während der Wärmebehandlung unter Einführung des Bandmaterials in eine heisse wässerige Lösung zum Zwecke der schnellen Abkühlung nach seiner Rekristallisationsbehandlung und wahlweise darauffolgender Einführung desselben in eine weitere wässerige heisse Lösung zwecks abschliessender Kühlung nach der Überalterungs-Wärmebehandlung, wobei die eine bzw. die andere dieser Lösungen als ein Phosphatierungsbad Anwendung finden.

Es wurde gefunden, daß das erfindungsgemäße Verfahren Ausführungsmöglichkeiten aufweist, die eine beliebige Regelung der Dicke und der Art des Phosphatfilms gestatten.

Nach einer ersten Ausführungsmöglichkeit des erfindungsgemäßen Verfahrens ist in dem Falle, wo eine Auflage von geringer Dicke mit hohem Phosphatgehalt erforderlich ist, eine einzige Eintauchung für die Dauer zwischen 0.5 und 40 Sekunden ausreichend.

Wenn in diesem Falle die Phosphatierungsbehandlung mit der sich an das Rekristallisationsglühen anschliessenden Abschreckung, jedoch ohne Vergütung bei zum Beispiel hochfestem Stahl, kombiniert wird, gelangt die Phosphatierung während der erwähnten Abschreckung zur Ausführung.

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Auf Grund dieser Erwägungen und Betrachtungen sei nunmehr eine spezielle Behandlung für Bleche näher erläutert, die zum Tiefziehen vorgesehen sind:

a) Erhitzung auf eine Temperatur oberhalb der Rekristallisationstemperatur des Bleches und Einhalten dieser Temperatur für eine ausreichende Zeitdauer, wobei diese Erhitzung und Vorwärmung unter Schutzgasatmosphäre durchgeführt werden;

b) Abschrecken in einem Phosphatierungsbad der vorbeschriebenen Art mit einer Temperatur von 80°C oder höher, wobei die Badverweilzeit zwischen 0.5 und 40 Sekunden bei einer unter 150°C liegenden Temperatur beträgt;

c) sehr gründliches Spülen des Bleches am Badausgang;

d) Vergüten oder Überalterungsbehandlung durch Erhitzen des Bleches auf einer Temperatur zwischen 300°C und 500°C.

Nach einer ersten Variante dieser Ausführungsform der Erfindung wird die abschliessende Kühlung in bekannter Weise derart durchgeführt, daß beispielsweise Strahlen der Umgebungsluft zur Einwirkung gebracht werden.

Nach einer zweiten Variante dieser Ausführungsform der Erfindung wird dann, wenn eine dicke Schutzschicht gegen Korosion erzeugt werden soll, das Band im Anschluss an die Überalterungsbehandlung erneut in einer Passivierungslösung abgeschreckt, die beispielsweise eine Mischung von $Cr^{3+}$ - $Cr^{6+}$ aufweist.

Leerseite

- 11 -

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| Nummer: | 29 09 698 |
| Int. Cl.2: | C 23 F 7/08 |
| Anmeldetag: | 12. März 1979 |
| Offenlegungstag: | 27. September 1979 |

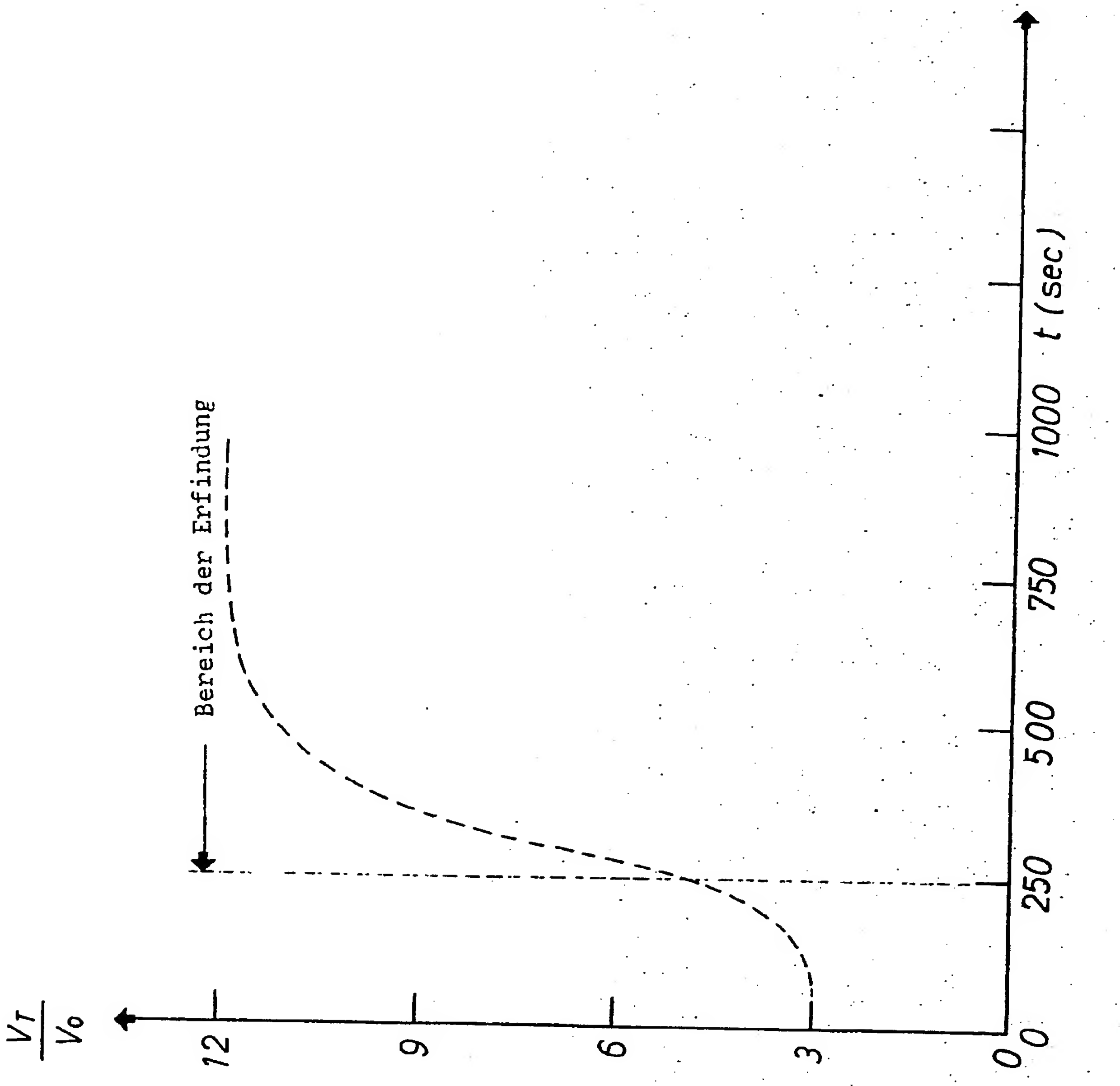


Fig. 1

909839/0738

02-B-190-A W

# PATENT SPECIFICATION

1,076,678

NO DRAWINGS

**1,076,678**

*Date of Application and filing Complete Specification June 29, 1965.*
*No. 27564/65.*

*Two Applications made in United States of America (Nos. 378,946 and 378,982) on June 29, 1964.*

*Complete Specification Published: July 19, 1967.*



**Index at acceptance:**—C7 U(4A, 4B, 4C, 4E1, 4E2A, 4E2B, 4E3, 4E4, 4F1, 4F2, 4G2, 4H1, 4H2, 4H4, 4H5, 4H7, 4H9, 4J, 4K, 4L, 4M1, 4M2, 4P, 4R, 5, 7A, 7C, 7G); B2 K(1A2, 1B1, 1B2, 1BY, 1C1, 2C, 2Y, 3C, 5D, 7A1, 7A3, 7AX, 7AY, 8D, 9K, 9P, 9Q7, 9Q10, 9QX, 9QY)

**Int. Cl.:**—C 23 f 7/00 // B 03 c

COMPLETE SPECIFICATION

## Improvements in the Coating of Metals

We, THE PYRENE COMPANY LIMITED, a British Company of, Great West Road, Brentford, Middlesex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is well known to form protective coatings on metal surfaces by treating the surfaces with conversion coating solutions containing materials which will react with the metal of the metal surface to form an insoluble coating. Such coatings are very frequently formed on surfaces of metals such as zinc, iron and aluminium. However, it is not always easy readily to produce coatings having satisfactory properties. For instance, on zinc it is often difficult to produce a coating which is sufficiently heavy and uniform. Also, conversion coatings formed on metal surfaces often are not very adherent, so that they do not form a satisfactory base for paint or other organic finish. In general these difficulties have been particularly marked when the metal surface to be coated is in the form of a continuously moving strip or sheet. In such instances it is clearly necessary that the coating formation should be accomplished in the minimum time possible.

Individual conversion coating processes are generally applicable only to one particular metal, but it often happens that it would be convenient to have a process suitable for treating a number of different metals without modification. Thus, it often happens that in installations which treat predominantly zinc surfaces, such as those resulting from electroplating or hot dip galvanising of steel or other ferrous surface it is desirable to treat also surfaces which are predominantly of iron or aluminium.

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According to the present invention a process for forming a protective coating on a metal surface comprises preheating the metal and spraying onto it a conversion coating solution of which the principal coating-forming ingredient is a coating phosphate, a coating oxalate, a coating acetate or phosphoric acid with an auxiliary acid, the temperature of the metal and the quantity of the solution applied being such that there is substantially no run-off of solution and a dry conversion coating is formed part of which at least is soluble, and then, without any intermediate rinsing step, rendering the coating totally insoluble by applying to it an insolubilising solution which reacts with the soluble components of the conversion coating to form insoluble products.

The metal surface onto which the solution is applied is preferably preheated to a temperature of at least 175°F, usually to a temperature of between 200 or 600°F or, more preferably between 275 and 425°F. The quantity of solution sprayed and the temperature of the metal are arranged such that there is substantially no liquid run-off from the surface, and it is found that a dry, substantially uniform coating may be formed. The solution is preferably sprayed in such a way that it is, in effect, applied as a mist, for example by gas atomisation such that the droplets of the mist have a size between 15 and 350 microns. Such a process is described in Specification No. 863,098. The conditions of operation are arranged in such processes that the droplets of coating solution deposited on the metal surface dry on the surface substantially in the positions in which they initially strike the surface.

The spraying may be conducted in any suitable manner, but the particular mode of operation will usually depend on the type

of articles being treated. Thus, small articles may be sprayed by hand, with one or more passes of the spray while articles in the form of strips or sheets may be passed continuously through one or more stationary spraying zones. When the metal surfaces to be sprayed are galvanised surfaces produced by hot galvanising it is particularly convenient to spray the surfaces while they are still hot from the galvanising.

The auxiliary acid included with phosphoric acid in the conversion coating solutions based on those two materials as the principal coating forming ingredients may be organic or inorganic. Examples of suitable acids are nitric acid, acrylic acid, methacrylic acid, polyacrylic acid, adipic acid, acetic acid, hydroxyacetic acid, gluconic acid, fumaric acid, maleic acid, malic acid, malonic acid, lactic acid, itaconic acid, tartaric acid, ethylene diamine tetraacetic acid, citric acid, hydroxymethyl phosphonic acid, oxalic acid, and chromic acid. Typically, these acids may be present in amounts to provide a ratio of $PO_4$ ions to acid in the range of about 100:1 to about 2:1, with amounts sufficient to provide a ratio of from about 10:1 to about 4:1 being preferred.

Materials which can be used as coating phosphates, oxalates and acetates for forming conversion coatings on metals are well known and generally comprise the phosphate, oxalate or acetate of a metal in an aqueous acidic solution. For example the principle coating forming ingredient may be zinc phosphate, ferrous phosphate, ferric phosphate, nickel phosphate, manganese phosphate, calcium phosphate, chromium phosphate, cobalt phosphate, aluminium phosphate, cadmium phosphate, or ferric oxalate. Mixed metallic phosphates such as zinc phosphate, zinc iron phosphate, zinc calcium phosphate, iron manganese phosphate, may also be used.

It is sometimes desirable to include in the conversion coating solution based on a coating phosphate auxiliary acid such as is listed above in amounts such as those mentioned. This inclusion is particularly desired when the conversion coating solution contains iron.

The conversion coating solutions generally contain from 0.1 to 10.0%, preferably 0.3 to 6.0%, by weight phosphate or phosphoric acid (measured as PO4).

In addition to coating phosphates or phosphoric acid and auxiliary acid the conversion coating solutions may also contain various other materials, for example accelerators. Such materials which may be included include nitrates, nitrites, sulphites, halides and halates, e.g. bromides, chlorates, bromates, perchlorates, iodates and periodates, peroxides, permanganates, organic nitro compounds such as m-nitrobenzene sulphonate, nitro guanidine, nitro methane, nitro ethane, 1-nitro propane, nitrobenzene, o-nitro benzaldehyde, p-nitrophenol, p-nitro aniline, p-nitrochloro benzene, and picric acid. Other additives which may be used in the composition are those which increase the etching tendency of the solution, such as the so-called double fluorides, including fluosilicates, fluoborates, fluotitanates, fluostannates, fluozirconates, and fluovanadates.

These additional materials are most conveniently added to an acidic solution of the coating phosphate or phosphoric acid in a form which is readily dispersible in the acidic aqueous solution. Many water dispersible forms of these compounds may be used provided they have no adverse effect on the coating composition, the metal substrate, or the coatings subsequently produced or applied. Typically, such additives may be present in the conversion coating composition in amounts within the range of 0.01 to 6.0 percent by weight, and desirably in amounts within the range of 0.02 to 4.0 percent by weight.

Conversion coating compositions based on coating phosphates are preferably used at pH values from 0.7 to 3.5 while those based on phosphoric acid are preferably used at pH values of from 0.3 to 5.5 and the solutions are preferably applied in such a manner so as to obtain a coating weight of phosphate ions of from 10 to 250 milligrams per square foot of metal surface being treated. Desirably, the coatings obtained contain phosphate in the range of about 20 to 100 milligrams per square foot.

Part at least of the conversion coatings produced in the invention are water soluble and the coatings are rendered insoluble by application of an insolubilising solution. A wide range of methods of effecting the insolubilisation may be used, it merely being necessary that the result shall be that it shall not be possible to dissolve out part of the resulting coating. Thus this step of insolubilising the coating can be considered to be one of immobilising or fixing the coating on the metal surface. The effect of this step is to make the previously applied phosphate coating more adherent to a subsequently applied paint or similar protective coating and/or to make it provide an improved barrier between the metal substrate and materials, for example water, with which it may come in contact and which are likely to be corrosive or to lift the paint from the surface. The reaction by which this fixing or immobilisation is accomplished may involve neutralization, double decomposition, esterification, resinification or organic complex formation. Generally two or more of these aspects may be present in each case.

Materials which may be used as the insolubilising ingredients of the insolubilising solution include salts of volatile acids, both organic and inorganic, preferably of metals having a valence of at least 2, although in

some instances salts of the alkali metals may be used, particularly where they are in complex salts which also contain metals having a valence of at least two. Specific salts which may be used include nitrates, carbonates, halides, and acetates. Examples of suitable metal cations in these salts are iron, both ferric and ferrous, zinc and chromium. Additionally, amines may also be used such as the fatty acid aliphatic amines and diamines wherein the fatty acids are derived predominantly from tallow or coconut oil, tertiary alkyl amines, hexamethylenediamine, monoethanolamine, and amides, such as those derived from the condensation of unsaturated fatty acids such as dilinoleic acid with aliphatic amines such as ethylene diamine. Oxides and hydroxides, preferably of metals having a valence of at least two may also be used. Typical of these materials are the zinc oxides, zinc hydroxides, iron hydroxides, both ferric and ferrous, chromium hydroxides, and silicon dioxide, preferably as colloidal silica. Additionally, metallic salt-oxide complexes may also be used such as pigments like zinc yellow, and zinc tetroxy chromate. Other materials which may be used include various organic resins or polymeric materials such as melamine acrylic resins, urea-formaldehyde and amine resins, urea-aldehyde resins, epoxys such as those prepared by the reaction of epichlorohydrin and bisphenol, polyvinylacetals, such as polyvinylbutyral, and dimethylhydantoin-formaldehyde resin. Preferably, these latter two materials, i.e., the metal salt oxide complexes or pigments and the resin materials, are used together rather than separately, and desirably in a weight ratio of resin to pigment greater than 1.5 : 1. Various organic reductants may also be used such as dimethylolurea, hexamethylolmelamine hydroquinone, pyrocatechol, pyrogallol, p-methylamino-phenyl sulphate, and N-p-hydroxyphenylglycine.

Trivalent chromium compounds such as chromium nitrate, chromium acetate, chromium carbonate, and chromium phosphate and organic complexes of trivalent chromium, such as methacrylato chromic chloride can also be used. Additionally, ammoniated oxides and ammoniated hydroxides of metals having a valence of at least two, for example, zinc, iron, both ferric and ferrous, and chromium, may also be used, either as such or in combination with colloidal silica. In many instances, with these materials, it is preferred also to include colloidal silica with the ammoniated oxide or hydroxide.

Various combinations of resins, such as polyvinyl butyral and a pigment, such as zinc tetroxy chromate have given excellent results. Dimethylhydantoin-formaldehyde resin with zinc yellow has also given good results. Typical concentrations of insolubilising ingredient, or mixture or ingredients, are from 0.1 to 6% by weight of the solution applied, with concentrations of from 0.3 to 1% preferred. Typical of the amount of insolubilising ingredient which may be deposited may be from 1 to 100 mg/sq. foot, while amounts of from 15 to 500 mg/sq. foot are preferred.

The insolubilising solution may be applied onto an unheated surface, for example a surface having a room temperature of, for example, from 65 to 75°F. Preferably however the surface onto which the composition is applied is preheated to a temperature of at least 175°F, preferably from 200 to 600°F although in general it is preferred that the upper limit on the temperature range should be below 350°F. The application may be effected by any convenient method, for example by roller coating, by immersing, by flooding or by spraying. However, the spraying technique described above and which results in there being substantially no run-off is the preferred method of application. Provided that the conditions of application are appropriate the insolubilising ingredients bring about insolubilisation of the unreacted ingredients of the coating very quickly, the insolubilisation generally being effected substantially simultaneously with the application of the solution.

It is well known that it is desirable to stabilise conversion coatings by treating them with a chromium-containing compound. This treatment, in conventional processes, generally takes the form of a chromate rinse. The stabilisation is carried out to improve the properties of the conversion coating. It is desirable to improve the properties of the conversion coatings formed in the process of the invention similarly, treating them with trivalent or hexavalent chromium as a stabiliser. The stabilising treatment may be effected by including a suitable chromium compound in the insolubilising solution or it may be effected by treating the coated surface with a chromium-containing stabilising solution subsequent to the insolubilisation of the coating. Examples of stabilising solutions which may be applied subsequently to the insolubilisation are acidic aqueous solutions or suspensions of chromates and dichromates of metals having a valency of at least two. Examples of such materials are zinc chromate and dichromate, aluminium chromate and dichromate, calcium chromate and dichromate, iron, both ferric and ferrous, chromate and dichromate, cobalt chromate and dichromate, and nickel chromate and dichromate. Additionally, in many instances, aqueous solutions of chromic acid ($CrO_3$) may also be used. The chromic acid may be used as such, or if desired it may be combined with other materials, such as aluminum oxide, colloidal silica, water glass, solution of zinc oxide and ammonium hydroxide, or solutions of

zinc oxide and ammonium hydroxide containing silica. These latter mixtures, of chromic acid combined with other materials, are examples of solutions which act both as insolubilising and as stabilising solutions. When solutions such as these are used it is generally only necessary to carry out a two stage process, although even if a chromium containing insolubilising solution is used it is sometimes desirable still to subject the surface to a stabilising treatment. Examples of other solutions which may be used to effect both insolubilisation and stabilisation of the conversion coating are solutions of resin compositions such as dimethyl hydantoin-formaldehyde resins containing pigment materials such as the zinc yellows and zinc tetroxy chromate, zinc bichromate with colloidal silica, and ferric hydroxide and colloidal silica compositions containing chromic acid.

In some instances trivalent chromium may be used as the stabilising material, examples of suitable trivalent materials being chromium salts such as chromium acetate, chromium phosphate, chromium nitrate, and chromium carbonate. Additionally, organic complexes of trivalent chromium, such as methacrylato chromium chloride may also be used. Generally such trivalent chromium materials are used in the insolubilising composition, so that the application of a separate stabilizing composition may not be essential. However, in some instances, particularly when the conversion coating solution was based on phosphoric acid and auxiliary acid, a subsequent chromate rinse may be very desirable. When a chromate stabilising composition is applied as a separate step the concentration of chromate, calculated as $CrO_3$, is typically from 0.01 to 2% by weight, while amounts of from 0.1 to 1% are preferred. The preferred weight of coating obtained by the stabilising treatment may typically be between 0.1 and 20 mg/sq. ft. while weights of from 1 to 8 mg/sq. ft. are preferred. When the chromium stabilising compound is included in the insolubilising solution it is preferred that it is included in such amounts as to yield the same coating weights of chromate. The application of a chromium stabilising solution may be effected in any convenient manner, for example by immersion or by roller application, although spraying methods are preferred. The application can be effected on unheated surfaces, for example surfaces having room temperatures of for example, 65 to 75°F., although preferably the surfaces are preheated to temperatures above 200°F, maximum temperatures of up to 400°F, or more preferably up to 350°F, being permissible. It is particularly preferred to carry out the application by the spraying process described in detail above with a surface temperature of above 200°F.

The process of the invention is most conveniently carried out by passing the articles to be coated continuously through a series of spray zones in which the articles are subjected to either two or three different spray treatments, depending on whether or not the chromium stabiliser is included in the insolubilising solution. The articles being treated may, for example, be galvanised surfaces produced immediately previously by a hot dip process and may be in the form of sheet or coil. Typical of the speed of travel of the metal articles which may be used are speeds of 10 to about 500 feet per minute.

The process of the invention has many advantages. It is a high speed process and it can be carried out so that there is no need to subject the conversion coating to a rinse. The process can be carried out so that all the reacting solutions being used are used up at once with the result that there is no recycling of them. As a result the control of the process is very simple, there being no necessity to continuously analyse the solutions being used. The corrosion and paint adhesion properties of the coatings produced by the invention are good and the coatings prevent white corrosion on storage of hot-dip galvanised articles. The corrosion and paint adhesion properties of the coatings do, however, vary to a certain extent from one process to another and from one metal article to another. A further advantage of the invention is that it is possible to subject galvanised articles having the coatings to a subsequent temper roller without any undue loss of quality of the coatings produced. The coatings produced by the invention prevent staining of zinc surfaces during storage.

To exemplify the invention conversion coatings were formed by the process of the invention on galvanised surfaces produced by a high speed continuous hot dip process and the coated surfaces were painted with an alkyd-melamine baking enamel paint and then subjected to corrosion and paint adhesion tests. In each process galvanised surfaces were cleaned with solvent and then heated to a temperature of from 275 to 325°F, generally about 300°F and coatings were then formed by the process of the invention using the spray technique described in detail above. The conversion coating solutions generally contained about 1% phosphate, measured as $PO_4$, and were applied to yield a conversion coating weight of from 40 to 50 mg/foot. The insolubilising solution generally had a concentration of 0.4 percent and was applied at a coating rate of 15 to 35 milligrams per square foot while the stabilizing composition generally had a $CrO_3$ content of 0.2 percent and was applied to yield a chromate coating weight of about 3 milligrams per square foot.

One test carried out was the salt spray test ASTM B117—61 with painted panels scribed as given in ASTM test D—165461. This uses a 5 percent sodium chloride fog. The ratings given depend on the creepage from the scratch, given in 1/16 of an inch. Ratings given as spot (S) indicate no creepage except in a small area. In the humidity test, panels were exposed in a walk-in room at 100 percent relative humidity at 100°F, for the designated period of time. The blistering was rated according to ASTM designation D714—56 and is reported as follows. D—dense; MD medium dense; M—medium; FM—few medium; F—few; and VF—very few. In both the salt spray and humidity tests, unless otherwise indicated, the exposure time was 504 hours. In the physical test, adhesion is determined by knife blade and the results are reported on the scale of 0 to 10, where 10 is excellent, 8 is good, 6 is fair, 4 is poor, 2 is very poor, 0 is complete loss of adhesion. In the forming test, painted panels were subjected to a severe deformation producing parallel short radius right angle bends and paired three dimensional short radius shoulders in one operation. Failures or degrees thereof are shown by percentage peeling of the paint.

The results are shown in the Table below.

For comparative purposes similar processes and tests were carried out in which an insolubilising coating step was omitted.

These examples are also included in the Table and are numbered with an X.

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 1 X | Zn and Ferrous phosphate solution content 0.1% Zn, 0.15% Fe, 1% $PO_4$ and 0.05% $HNO_3$ | — | 0.2% aqueous solution of $CrO_3$ | 1—3 | — | 6—5 | — |
| 2 | Same as 1 | Solution of 0.4% ZnO in an 18:82 dilution of conc. $NH_4OH$ in water also containing 0.2% $CrO_3$ and 0.3% colloidal $SiO_2$ | — | 0—1 | — | 9 | — |
| 3 | Same as 1 | $ZnCr_2O_7$ (aqueous solution containing 0.2% $CrO_3$) | — | 1—4 | F | 7—6 | 35 |
| 4 | Same as 1 | Same as 3 plus 0.3% colloidal $SiO_2$ | — | 0—1 | F | 10 | 23 |
| 5 X | Same as 1 but with 0.25% $HNO_3$ | — | 0.2% aqueous solution of $CrO_3$ | 1—5 | M | 6—4 | 65 |
| 6 | Same as 5 | 1.5% aqueous solution of dimethylhydantoin formaldehyde resin | 0.2% aqueous solution of $CrO_3$ | 0—3 | F | 10 | 2.5 |
| 7 | Zn phosphate solution as disclosed in United States Patent No. 2,835,617 | 0.8% aqueous solution of melamine-formaldehyde resin | 0.2% aqueous solution of $CrO_3$ | — | — | 10 | 0 |
| 8 | Ferrous phosphate sol. containing 1% $PO_4$ and 0.25% $NO_3$ and 0.15% Fe | 0.05% aqueous sol. of N-P-hydroxyphenyl glycine | 0.2% aqueous solution of $CrO_3$ | — | — | 8 | 10 |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 9 X | Same as 8 | — | Same as 8 | — | — | 6 | 50 |
| 10 | Same as 5 | Same as 2 but without $SiO_2$ | — | 0—1 | — | 10 | 2.5 |
| 11 | Same as 5 | High molecular weight amine sold under the Trade Mark Amberlite LA—1 | 0.2% aqueous solution of $CrO_3$ | 1—3 | — | 10 | 0 |
| 12 X | Same as 8 | — | Same as 8 | — | (336 hours) D | 9 | 55 |
| 13 | Same as 8 | 0.2% aqueous solution of $Fe(NO_3)_3.9H_2O$ | Same as 11 | — | M | 10 | 23 |
| 14 X | Same as 5 | — | Same as 5 | — | — | 6—5 | 20 |
| 15 | Same as 5 | 0.3% aqueous dispersion of $CrPO_4$ | Same as 5 | — | — | 10 | 10 |
| 16 | Same as 5 | 0.3% aqueous dispersion of colloidal $SiO_2$ | Same as 5 | — | — | 10 | 13 |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 17 | Same as 5 | 0.3% aqueous dispersion of $Al_2O_3$ | Same as 5 | — | — | 10 | 5 |
| 18 | Same as 5 | Same as 2 without $CrO_3$ and $SiO_2$ | Same as 5 | 0—1 | F | 9—7 | 38 |
| 19 | Same as 5 | Same as 2 without $SiO_2$ | — | 0—1 | F | 10—8 | 28 |
| 20 | Same as 5 | Same as 2 without $CrO_3$ | Same as 5 | 0—1[B] | VF | 10 | 25 |
| 21 | Same as 5 | Same as 2 | — | 0—1[B] | FM | 10 | 10 |
| 22 | Same as 5 | — | Same as 5 | 1—2 | MD (336 hours) | 7—4 | — |
| 23 | Same as 5 | 0.4% aqueous suspension of ZnO | Same as 5 | 0—2 | FM | 10 | 13 |
| 24 | Same as 5 | 0.8% aqueous suspension of $ZnCO_3$ | Same as 5 | 0—1 | VF | 10 | 28 |

In the following examples 25 to 28, a post-forming vinyl paint was substituted for the alkyd-melamine baking enamel prior to running the comparative tests.

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 25 | Same as 5 | 0.4% aqueous suspension of $Fe(OH)_3$ | Same as 5 | — | — | 10 | 0 |
| 26 | Same as 5 | Same as 28 plus 0.3% colloidal $SiO_2$ | Same as 5 | — | — | 10 | 25 |
| 27 | Same as 5 | Same as 29 plus 0.2% $CrO_3$ | — | — | — | 10 | 0 |
| 28 | Same as 5 | — | Same as 5 | — | — | 7 | 0 |
| 29 | Same as 5 | — | Same as 5 | 1—2 | (396 hours) MD | 7—4 | — |
| 30 | Same as 5 | 0.2% aqueous dispersion of $Ba(OH)_2$ | Same as 5 | (336 hours) 0—3 | MD | 10 | — |
| 31 X | Same as 5 | — | 0.2% $CrO_3$ | — | — | 8 | 35 |
| 32 | Same as 5 | Aqueous solution of 0.2% $CrO_3$ and 0.3% colloidal $SiO_2$ | — | — | — | 10 | 15 |
| 33 | Same as 5 | Same as 35 except 0.3% $SiO_2$ present as a potassium silicate | — | — | — | 10 | 2.5 |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 34 | Same as 5 | Aqueous solution of 0.05% pyrocatechol and 0.3% colloidal $SiO_2$ | 0.2% $CrO_3$ | — | — | 9—5 | 7.5 |
| 35 | Same as 5 | Aqueous solution of 0.05% ethylene glycol and 0.3% colloidal $SiO_2$ | 0.2% $CrO_3$ | — | — | 10 | 5 |
| 36 | Same as 8 | Aqueous dispersion containing 0.5% polyvinyl butyral and 0.5% zinc tetroxy chromate | — | — | F | 10 | 0 |
| 37 | Same as 8 | Same as 39 except with copolymer of butadiene and styrene | — | — | MD | 10—9 | 2—5 |
| 38 | Same as 8 | Same as 39 except with copolymer of styrene and polyvinyl pyrollidone | — | — | FM | 10 | 0 |
| 39 | Same as 8 | Aqueous dispersion of 0.5% dimethylol urea and 0.2% of $CrO_3$ as $Cr_2(Cr_2O_7)_3$ | — | 0—1 | F | 8 | 5 |
| 40 | Same as 8 | Aqueous dispersion of 0.5% melamine-formaldehyde resin and 0.5% of zinc yellow ($KO_2.4Z_n$ 0.4 $CrO_3.3H_2O$) | — | 0—1 | VF | 10 | 2.5 |
| 41 X | Same as 8 | — | 0.2% $CrO_3$ | 1—2 | F | 5 | 85 |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 42 | Same as 8 | Aqueous dispersion of 1.5% dimethylhydantoin-formaldehyde resin and 0.5% zinc yellow | — | — | — | 9 | — |
| 43 X | Zn—Ni solution containing 1.0% $PO_4$, 0.5% $NO_3$ and 0.45% total Zn and Ni | — | Aqueous solution of 0.2% $CrO_3$ | (168 hours) 1—2 | (48 hours) D | 7 | 35 |
| 44 | Same as 43 | Same as 2 without $CrO_3$ | Same as 43 | 0—2[s] | VF | 10 | 5 |
| 45 X | Zn—Fe solution containing 1.0% $PO_4$, 0.25% $NO_3$ and 0.1—0.3% Zn and Fe | — | Same as 43 | 1—1 | FM | 9 | 2.5 |
| 46 | Same as 45 | Same as 44 | Same as 43 | 0—1[s] | VF | 10 | 0 |
| 47 X | Same as 45 except Ca substituted for Fe | — | Same as 43 | 1—3 | (48 hours) D | 9 | 15 |
| 48 | Same as 47 | Same as 44 | Same as 43 | 0—3[s] | F | 10 | 10 |
| 49 X | Same as 45 except Mn substituted for Zn and Fe | — | Same as 43 | 1—2 | FM | 8 | 10 |
| 50 | Same as 49 | Same as 44 | Same as 43 | 0—1[s] | F | 10 | 15 |
| 51 X | Same as 49 except Ni substituted for Mn | — | Same as 43 | (168 hours) 1—3 | (48 hours) D | 8 | 7.5 |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 52 | Same as 51 | Same as 44 | Same as 43 | 10 | (336 hours) M | 10 | 2.5 |
| 53 X | Same as 49 except Ca substituted for Mn | — | Same as 49 | 2—3 | (48 hours) D | 9 | 43 |
| 54 | Same as 53 | Same as 44 | Same as 53 | $0—2^{8}$ | FM | 10 | 45 |
| 55 | Same as 5 | Same as 44 | Same as 6 | $0—3^{9}$ | VF | 9.5 | 2.5 |
| 56 | Same as 5 except glycolic acid instead of $HNO_3$ | Same as 44 | Same as 6 | $0—1^{8}$ | VF | 10 | 30 |
| 57 | Same as 5 except acrylic acid instead of $HNO_3$ | Same as 44 | Same as 6 | $0—1^{8}$ | VF | 9 | 45 |
| 58 | Same as 5 except adipic acid instead of $HNO_3$ | Same as 44 | Same as 6 | $0—3^{8}$ | VF | 10 | 40 |
| 59 | Same as 5 except hydroxy-methyl phosphonic acid instead of $HNO_3$ | Same as 44 | Same as 6 | $0—1^{8}$ | VF | 9—10 | 40 |
| 60 | 1.0% hydroxymethyl phosphonic acid containing 0.14% Fe | Same as 55 | Same as 6 | — | — | 9—10 | — |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 61 X | Aqueous solution of 1% $H_3PO_4$ and 0.05% $HNO_3$ | — | Aqueous solution of 0.2% $CRO_3$ | (48 hrs.) 1—3 | (48 hrs.) MD | 7 | 45 |
| 62 | Same as 61 | 18:82 dilution of concentrated $NH_4OH$ in $H_2O$ and containing 0.4% ZnO | Same as 61 | 0—1 | M | 10—9 | 40 |
| 63 X | Same as 61 but with 0.25% $HNO_3$ | — | Same as 61 | 0—1 5 S | (48 hrs.) D | 2 | 85 |
| 64 | Same as 63 | 0.4% suspension of $CrPO_4$ | Same as 61 | 0—1 | F | 10 | 64 |
| 65 | Same as 63 | Aqueous dispersion containing 0.8% polyvinyl butyral and 0.5% zinc yellow | — | 0—1 4 S | VF | 7 | 75 |
| 66 | Same as 63 | Same as 62 plus 0.3% SiO and 0.2% $CrO_3$ | — | 0—1 S | (48 hrs.) D | 9 | 75 |
| 67 | Same as 63 | Aqueous dispersion of 1.5% dimethyl hydantoin formaldehyde resin and 0.5% zinc yellow | — | 1—3 | (48 hrs.) D | 8 | 78 |

| Example | Conversion Coating Solution | Insolubilising Solution | Stabilising Coating Solution | Salt Spray | Humidity | Knife Adhesion | Forming (% Peel) |
|---|---|---|---|---|---|---|---|
| 68 | Same as 61 | Same as 62 plus 0.3% $SiO_2$ | Same as 61 | 0—1 S | FM | 4 | 98 |
| 69 X | Same as 61 | — | Same as 61 | (168 hrs.) 1—2 5 S | D | 6 | 25 |
| 70 | Same as 61 | Aqueous dispersion of 3.0% dimethyl hydantoin formaldehyde resin | Same as 61 | 1—2 | D | 9 | 5 |
| 71 X | Same as 61 | — | Same as 61 | (48 Hrs.) 1—2 3 S | (168 Hrs.) D | 5 | 53 |
| 72 | Same as 61 | Same as 62 plus 0.2% $CrO_3$ | — | 0—3 S | FM | 8 | 55 |
| 73 X | Same as 61 | — | Same as 61 | 0—2 4 S | (24 Hrs.) | 5 | 75 |
| 74 | Same as 61 | Aqueous dispersion of 0.3% $SiO_2$ and 0.2% $CrO_3$ | — | (168 Hrs.) 0—3 4 S | MD | 7 | 63 |
| 75 | Same as 61 | Same as 62 | Aqueous dispersion of 0.3% SiO and 0.2% $CrO_3$ | 1—2 3 S | (48 Hrs.) D | 9 | 2.5 |
| 76 | Same as 61 | Same as 62 | Same as 75 with sodium silicate substituted for $SiO_2$ | 0—3 4 S | (48 hrs.) | 9 | 50 |
| 77 | Same as 61 | Same as 68 with sodium silicate substituted for $SiO_2$ | Same as 61 | 0—1 | (24 hrs.) D | 8 | 20 |

EXAMPLE 78

The procedures of Examples 36, 37 and 38 were repeated with the exception that the coating compositions were applied to panels of cold rolled steel, rather than zinc panels. Additionally, in the case of Example 36, the quantities of the components of the immobilizing coating composition were quadrupled and in the case of Examples 37 and 38, the amounts of these components were doubled. In each instance, the knife adhesion and forming test results were 10 and 0, respectively.

EXAMPLE 79

A series of runs was made wherein the conversion coating was an aqueous solution containing from 0.1 to 0.5 percent acetic acid and oxalic acid in the amounts of 0.1, 0.2, 0.5, and 1 percent. In the four runs made, the temperatures of the galvanised panels onto which the coating was misted were 200°F, 250°F, 300°F, and 375°F. In each instance, the application of the conversion coating material was followed by a mist-on application of a 0.2 percent aqueous solution of $CrO_3$. The typical results obtained on testing the painted panels showed from 0 to 3 creepage after 504 hours in the salt spray, blister failure only after 504 hours in the humidity test and fair to good knife adhesion and forming tests.

EXAMPLE 80

The procedure of Example 79 was repeated with the exception that the conversion coating composition was a ferric oxalate solution containing 0.5 percent iron which was applied to panels which were at a temperature of 375°F. The test results on the painted panels showed good humidity and physical test ratings.

EXAMPLE 81

Galvanised panels were preheated to provide surfaces at 300°F. The ferrous phosphate conversion coating solution of Example 5 was then misted onto these surfaces in a series of runs designed to obtain a wide range of coating weights on the surface. In the first series of runs, the number of passes of the spray gun over the surface was varied from 1 to 4 and the coating weights obtained varied in the amount of $PO_4$ from 29 to 86 milligrams per square foot. In the next series of runs, the times for each pass over the panels were varied from 1—6 seconds and coating weight variations, in terms of $PO_4$ content were obtained within the range of about 14 to about 83 milligrams per square foot. In the third series, the $PO_4$ concentration of the ferrous phosphate solution was varied within the range of about 0.5 to about 5 percent and there were obtained coating weights within the range of about 20 to about 250 milligrams $PO_4$ per square foot. Thereafter, in each instance, an aqueous $CrO_3$ solution was misted onto the panels to provide a coating containing 3 milligrams per square foot of $CrO_3$. The paint bonding performances of the surfaces produced were then evaluated and in all instances, these were acceptable although better paint bonding was obtained when the $PO_4$ coating weight was within the range of about 20 to about 100 milligrams per square foot.

EXAMPLE 82

The procedure of the preceding Example was repeated several times using the following temperatures of the zinc metal surface being coated: 175°, 200°, 225°, 275°, 300°, 325°, 375°, 400°, 425° and 500°F. In each instance, an excellent coating was obtained, although at the lowest temperatures of 175°F, the coating was somewhat spotted.

EXAMPLE 83

The procedure of Example 20 was repeated using the same conversion coating composition followed by the immobilizing composition of Example 20 and the stabilizing composition of Example 6. In this example, however, these coatings were applied to panels of cold rolled steel and aluminium, rather than zinc. In each instance, the coating obtained gave very good results in the salt spray and humidity test and a 10 rating in the knife adhesion and no peeling in forming tests were obtained, respectively.

EXAMPLE 84

A phosphate composition which was .01 molar Zn, .01 molar Ni, 0.1 molar $PO_4$, 0.04 molar $NO_3$ was misted onto commercial galvanised panels to provide 40—50 milligrams $PO_4$ per square foot, after which a fixer solution containing 1.5 percent dimethylhydantoin-formaldehyde resin and sufficient zinc dichromate to give 0.2 percent $CrO_3$ was misted on, at a rate to provide 3 milligrams $CrO_3$ per square foot. The panels were then painted with a vinyl baking paint and excellent salt spray, humidity and physical tests were obtained as shown below:

| | Salt Spray | Humidity | Adhesion | Forming |
|---|---|---|---|---|
| Zincdichromate control | N,* | VF, F | 3 | 80% peel |
| DMHF Zinc dichromate | N,N | VF, F | 10 | 0 |

N = zero creepage

* failed in 48 hrs. (major peeling)

EXAMPLE 85

A ferrous phosphate solution containing 1.8% $PO_4$, 0.25% $NO_3$, 0.15% Fe was misted on 300°F galvanised panels to give 40—50 milligrams $PO_4$ per square foot and was followed by an aqueous resin soluble chromate composition, misted on to provide 3 milligrams $CrO_3$ per square foot. This latter composition contained 1.5 percent dimethylhydantoin-formaldehyde resin and sufficient zinc dichromate solution to give 0.2 percent $CrO_3$. On panels painted with a high temperature baking vinyl, this treatment improved the knife adhesion from 7 to 10, when compared to the use of zinc dichromate without the resin present.

EXAMPLE 86

A series of zinc and nickel phosphate solutions were misted onto commercial galvanised panels at 300°F in an amount to obtain a coating weight of 40—50 milligrams $PO_4$ per square foot.

The metal content of the phosphate solutions was .02 molar with approximately 0.1 molar $PO_4$ and 0.04 molar $NO_3$. The Zn/Ni ratio was varied as follows: 1:0, 2;1, 1;1, 1;2, and 0:1. A further variant was introduced by adding $H_2SiF_6$ at 0.0 to 0.2 percent.

The phosphate coasting was followed quickly with a fixer prepared from: zinc yellow pigment 0.5%; $SiO_2$ 0.05% dimethylhydantoin-formaldehyde resin 1.5%.

This composition was misted to provide approximately 3 milligrams $CrO_3$ per square foot.

These coatings were painted with a high temperature vinyl composition. All variants showed excellent performance in accelerated and physical tests.

A similar series was made with the metal level raised to 0.05 molar also with excellent results.

The process of Examples 61 to 77 have been repeated using other auxiliary acids including chromic acid, glycolic acid, acrylic acid, adipic acid, hydroxymethyl phosphonic acid and other insolubilising materials including tertiary alkyl amines, hexamethylene diamine, monoethanol amine, butanol, polypropylene glycol, resorcinol, dimethylol urea, hexamethylol melamine, hydroquinone, pyrogallol and ammoniated iron oxide and the like, applied both to metal heated before and after the application of the conversion coating, using roll-on and immersion techniques as well as spraying techniques, and comparable results were obtained.

WHAT WE CLAIM IS:—

1. A process for forming a protective coating on a metal surface which comprises preheating the metal and spraying onto it a conversion coating solution of which the principal coating-forming ingredient is a coating phosphate, a coating oxalate, a coating acetate or phosphoric acid with an auxiliary acid, the temperature of the metal and the quantity of the solution applied being such that there is substantially no run-off of solution and a dry conversion coating is formed part of which at least is soluble, and then, without any intermediate rinsing step, rendering the coating totally insoluble by applying to it an insolubilising solution which reacts with the soluble components of the conversion coating to form insoluble products.

2. A process according to claim 1 in which the insolubilising solution contains trivalent or hexavalent chromium.

3. A process according to claim 1 in which the protective coating formed is subsequently treated with a solution containing hexavalent chromium.

4. A process for forming a protective coating on a metal surface which comprises preheating the metal and spraying onto it a conversion coating solution of which the principal coating-forming ingredients is a coating phosphate or is phosphoric acid with an auxiliary acid, the temperature of the metal and the quantity of the solution applied being such that there is substantially no run-off of solution and a dry phosphate conversion coating is formed in which there remains unreacted, soluble coating-forming ingredient, and then, without any intermediate rinsing step, rendering the coating totally insoluble by applying to it an insolubilising solution which reacts with the unreacted coating-forming ingredient by double decomposition, neutralisation, esterification, resinification or organic complex formation to form insoluble products, the protective coating being stabilised

by including trivalent or hexavalent chromium in the insolubilising solution or by subsequently treating it with a solution containing hexavalent chromium.

5. A process according to any one of the preceding claims in which the metal surface is a zinc surface.

6. A process according to claim 5 in which the zinc surface is formed by hot galvanising a ferrous surface and the conversion coating solution is applied to the galvanised surface while this is still hot from the galvanising.

7. A process according to claim 6 in which the protective coating is subsequently stabilised by spraying it with a solution containing hexavalent chromium while the surface is still hot.

8. A process according to any one of the preceding claims in which the conversion coating solution contains from 0.3 to 6.0% by weight of coating phosphate, (measured as $PO_4$).

9. A process according to any one of claims 1 to 7 in which the conversion coating solution contains from 0.3 to 6.0% by weight of phosphoric acid (measured as $PO_4$) and contains also an auxiliary acid in a proportion of phosphoric acid to auxiliary acid of from 100:1 to 2:1.

10. A process according to claim 9 in which the proportion of phosphoric acid to auxiliary acid is from 10:1 to 4:1.

11. A process according to any one of the preceding claims in which the auxiliary acid is nitric acid.

12. A process according to any one of the preceding claims in which the conversion coating solution additionally contains an accelerator.

13. A process according to any one of the preceding claims in which the insolubilising solution contains as insolubilising ingredient a salt of a metal having a valency of greater than 2 with a volatile acid, an ammoniated oxide or hydroxide of such a metal, a metal salt-oxide complex, an amine, an organic resin, a mono-, di-, or polyhydroxy alcohol, an organic reductant, or an organic complex of trivalent chromium.

14. A process according to any one of claims 1 to 12 in which the insolubilising solution contains as insolubilising ingredient colloidal silica, alone or with other insolubilising ingredients.

15. A process according to claim 13 in which the insolubilising ingredient is zinc oxide or zinc hydroxide dissolved in ammonia.

16. A process according to claim 15 in which the solution additionally contain colloidal silica.

17. A process according to claim 13 in which the insolubilising coating solution is an aqueous solution of dimethyl hydantoin-formaldehyde resin.

18. A process according to claim 17 in which the aqueous solution additionally contains zinc yellow pigment.

19. A process according to claim 1 substantially as herein described with reference to any one of the Examples.

20. Articles coated with a protective coating by a process according to any preceding claim.

For the Applicants:—
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52, Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

02-B-190-A 1

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 781 860 A1

(12) **EUROPÄISCHE PATENTANMELDUNG**

(43) Veröffentlichungstag:
02.07.1997 Patentblatt 1997/27

(51) Int Cl.6: **C23C 22/68**, C23C 8/16

(21) Anmeldenummer: 96810886.0

(22) Anmeldetag: 20.12.1996

(84) Benannte Vertragsstaaten:
AT DE FR IT NL

(30) Priorität: 23.12.1995 DE 19548740

(71) Anmelder: ABB RESEARCH LTD.
8050 Zürich (CH)

(72) Erfinder: Förster, Stefan, Dr.
8152 Opfikon (CH)

(74) Vertreter: Pöpper, Evamaria, Dr. et al
Asea Brown Boveri AG
Immaterialgüterrecht(TEI)
Haselstrasse 16/699 I
5401 Baden (CH)

(54) **Verfahren zur Oberflächenbehandlung von Aluminium und Aluminiumlegierungen**

(57) Bei einem Verfahren zur Oberflächenbehandlung von Aluminium und Aluminiumlegierungen für mechanisch hochfeste Verbindungen mit Reaktionsharzsystemen, wobei die Metall- bzw. Legierungsoberfläche zunächst mechanisch aufgerauht und entfettet werden und nachfolgend das Aluminium bzw. die Aluminiumlegierungen in Wasser bei Temperaturen oberhalb der Raumtemperatur hydratisiert werden, wird nach der Hydratisierung eine Wärmebehandlung durchgeführt. Dabei werden das Aluminium bei Temperaturen oberhalb Raumtemperatur bis maximal 500 °C und die Aluminiumlegierungen bei Temperaturen im Bereich der Ausscheidungshärtung der jeweiligen Aluminiumlegierung wärmebehandelt. Zusätzlich kann daran anschliessend eine Behandlung der metallischen Substrate in einer Lösung mit 0,01 bis 2,0 Gew.% einer metallorganischen Substanz erfolgen. Es bildet sich eine thermisch stabile, feine Oberflächenstruktur mit einer hohen chemischen Affinität zu den Reaktionsharzsystemen aus, so dass das Verbundsystem eine hohe Haftzugfestigkeit besitzt.

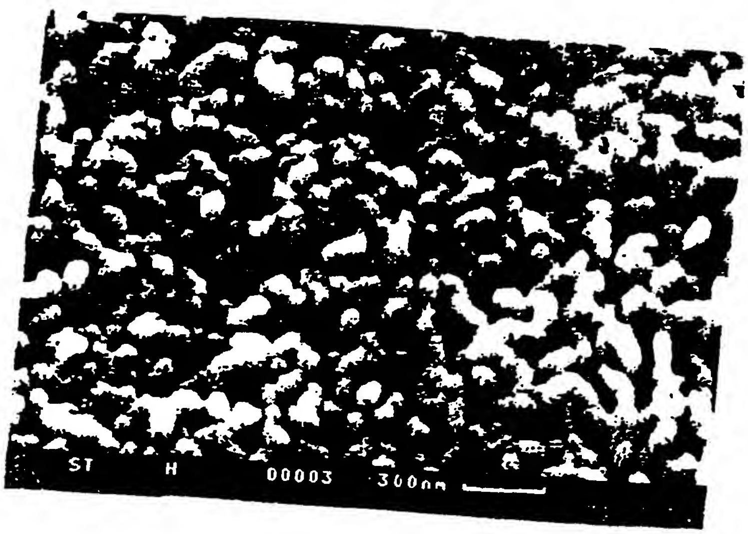


FIG. 4

EP 0 781 860 A1

## Beschreibung

### Technisches Gebiet

Die Erfindung bezieht sich auf das Gebiet der Werkstofftechnik. Sie betrifft ein Verfahren zur Oberflächenbehandlung von Aluminium und Aluminiumlegierungen, welches geeignet ist, mechanisch hochfeste Verbindungen mit Reaktionsharzsystemen zu erzielen.

### Stand der Technik

Im Mittel- und Hochspannungsbereich werden polymere Isolationskomponenten mit metallischen Eingusselektroden verwendet. Der Stromträger besteht vorwiegend aus Aluminium, während der Isolationswerkstoff aus einem mit Mineralpulver gefüllten Epoxidharz besteht. Die Grenzfläche zwischen Aluminium und Epoxidharz wird mechanisch und elektrisch hoch belastet, deshalb ist für eine volle Funktionsfähigkeit sowohl im Kurzzeit- als auch im Langzeitverhalten eine hohe Haftfestigkeit des Epoxidharzes auf dem metallischen Grundkörper unabdingbare Voraussetzung.

Für die Erzielung hoher Haftfestigkeiten müssen zahlreiche Bedingungen erfüllt werden. Zum einen muss die Metalloberfläche mechanisch aufgerauht werden. Zur weiteren Verzahnung muss ausserdem eine hochporöse Oberflächenmorphologie erzeugt werden, die zusätzlich eine hohe chemische Affinität zum Reaktionsharz aufweisen muss.

Die mechanische Aufrauhung der Oberfläche ist bekannter Stand der Technik und erfolgt beispielsweise mittels Sandstrahlen, an das sich ein Entfetten anschliesst.

Für die Erzeugung der benötigten hochporösen Oberflächenschichten werden bisher elektrochemische Verfahren verwendet. Bekannt ist das Anodisieren in verschiedenen Säuren, z.B. in Phosphor-, Chrom- oder Schwefelsäure. Diese Verfahren haben den Nachteil, dass sie einerseits mit hohen Kosten verbunden sind und andererseits die Umwelt stark belasten und deshalb aus ökologischen Gründen unerwünscht sind.

In der Literatur sind Angaben zu finden über Oberflächenbehandlungen von Aluminium bzw. Aluminiumlegierungen mit Wasser im Hinblick auf Verbindungen zu polymeren Materialien, wie Thermoplasten und Duromeren. Als Beispiele werden genannt:

Arslanov, V.V.; Funke, W.: "The effect of water on the adhesion of organic coatings on aluminium", Prog. Org. Coatings 15, 1988 (4), S. 355-363,
Iwama, T.; Katsumata, K.; Takeuchi,Y.: "Effect of the method of hydration treatment on the adhesion of coating films to aluminium", J. Met. Finish. Soc. Jpn. 37, 1986 (9), S. 569-574,
Davies, R.J.: "The morphology and properties of aluminium oxides before and after exposure to water", Adhesion'87, Proceedings of the 3rd International Conference, York, 1987, S. G/1-G/5, 9(12)4,
McCarvil, W.T.; Bell, J.P.: "The effect of time and type of water pretreatment on bond strength of epoxy-aluminium joints", J. Appl. Polym. Sci., 18, 1974 (2), S. 335-342.

In diesen Schriften sind Untersuchungsergebnisse dargestellt, die sich auf Folien bzw. Schichtverbunde zwischen Aluminium bzw. Aluminiumlegierungen und Copolymeren auf der Basis von Polyethylen sowie Epoxidharzen beziehen. Die Hydratisierungen wurden bei Raumtemperatur in verschiedenen wässrigen Medien, z.B. Wasserglaslösungen durchgeführt. Allen Arbeiten gemeinsam ist die Bildung einer Hydratschicht mit einer charakteristischen Oberflächenmorphologie. Die Anwendungen erfolgten bei Raumtemperatur. Es wurde festgestellt, dass bei einer Hydratisierung bei Raumtemperatur mit zunehmender Hydratisierungszeit nach einer anfänglichen Reduktion der Haftfestigkeit diese danach ansteigt. Der Nachteil dieser bei Raumtemperatur hydratisierten Schichten besteht darin, dass sie bei erhöhten Temperaturen (>100°C) thermisch nicht stabil sind.

Aus S. Wernick und R. Pinner: "Die Oberflächenbehandlung von Aluminium", Eugen G. Lenze Verlag, Saalgau/ Württ., Germany, 1969, S. 178-179 ist bekannt, dass auf Aluminiumoberflächen dichte Böhmit-Überzüge durch Kochen in destilliertem Wasser bei 75 bis 120 °C erzeugt werden können, wobei Verunreinigungen des Wassers die Filmbildung beeinträchtigen können.

In DE 43 03 339 C2 wird ein Verfahren zur Behandlung von Aluminiumdruckgussteilen vor dem Aufbringen eines porösen, katalytischen Überzuges beschrieben, mit dem die Haftungseigenschaften der Aluminiumdruckgussteile derart verbessert werden, dass offenporige anorganische Überzüge auch unter korrosiven Umgebungsbedingungen dauerhaft auf der Oberfläche anhaften. Nach einer Entfettung und Strahlbehandlung werden die Aluminiumdruckgussteile in entionisierten Wasser bei Temperaturen zwischen 90 und 100 °C im Zeitraum von 0,5 bis 1 Stunde mit einer 0,5 bis 1 µm dicken Böhmitschicht versehen.

Diese Verfahren zur Oberflächenbehandlung von Aluminium und seinen Legierungen sind nicht ausreichend, um hohe Haftfestigkeiten dieser metallischen Werkstoffe mit organischen Reaktionsharzsystemen auch bei erhöhten Temperaturen zu erreichen.